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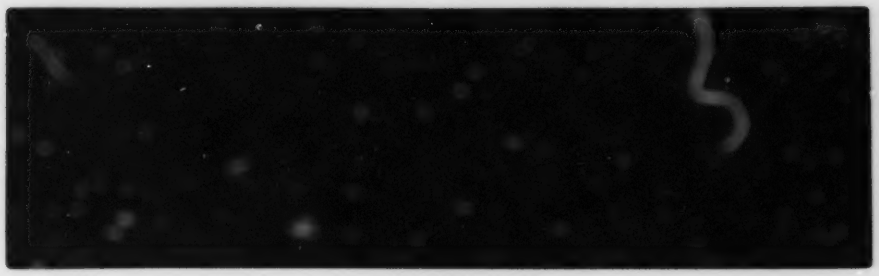

Canada

LASER PROCESSING OF CATALYTIC MATERIALS

Part 1

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PART 1

by

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Abstract

Catalyst materials have been subjected to thermal processing by radiation from a low power CW CO_2 laser. This new method of catalyst processing has been shown to be particularly useful for regeneration of coked-spent hydrodesulphurization catalysts. The regeneration process requires intensities of about 50 W/cm^2 with multiple particle irradiation dwell times, each of the order of a second duration. A laser regeneration unit capable of processing 150 g batches of spent catalyst extrudates was constructed and tested. Catalysts regenerated with this novel process were examined by mercury porosimetry, elemental analysis by Proton Induced X-ray Emission (PIXE), Fourier Transform Infra-red Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). Laser regenerated materials were shown to be equivalent to materials processed by conventional means, but the total processing time was much reduced. Comparison of energy consumption to regeneration in a conventional furnace of approximately the same capacity shows an advantage in efficiency in the laser method.

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Chapter 1

Introduction

As the world's supply of crude shifts to poorer, heavier stocks containing nitrogen, sulphur and heavy-metals, hydrotreating catalysts are increasingly used to remove potential pollutants and catalyst poisons. Ni/Mo and Co/Mo catalysts are presently used extensively by the petroleum industry for the removal of organic sulphur and nitrogen components from refinery feedstocks. Hydrodesulphurization (HDS) using these catalysts is a fascinating process. Sulphur and nitrogen are efficiently removed from large, complex molecules in a harsh environment, which inevitably leads to catalyst deactivation.

Large asphaltenic molecules typically present in heavy feedstocks are slow to diffuse through the catalyst and contribute to extensive coking (accumulation of carbonaceous deposit) early in the run cycle. This fouling mechanism may be accelerated by the presence of Lewis base groups in some of these molecules which form strong bonds with acidic sites in the catalyst surface. The presence of compounds containing vanadium and other heavy metals may lead to extensive pore plugging and active site blockage, another source of deactivation. A schematic plot showing the influence of coke formation and metals deposition as a hydrotreating catalyst ages is given in figure 1.1.

As the catalyst ages, these and other deactivating processes, necessitate an increase in reaction temperature to maintain adequate reaction rates. Eventually catalytic activity falls below an acceptable level, and the decision to shut down and replace the catalyst is made. The typical lifetime of hydrotreating catalysts,

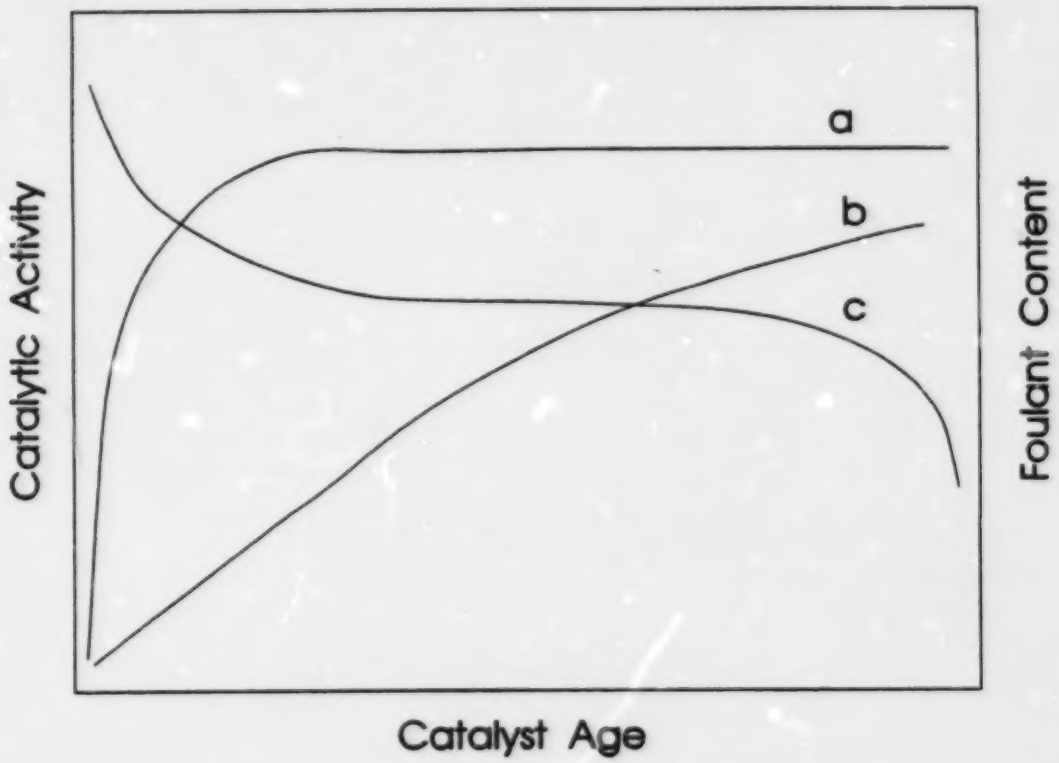


Figure 1.1: Schematic plot showing correlation of catalytic activity with coke formation and metals deposition; after Thakur and Thomas (1985). a) Coke formation, b) Metal deposition c) Catalytic activity

when used with heavier, poorer feedstocks, is less than 18 months. Generally, the operation of hydroprocessing in fossil fuels production constitutes a major cost in the conversion of primary hydrocarbons to refined fuel products. The catalyst inventory is a significant portion of this overall cost and requires careful maintenance.

Coke formation on the active surface is the major cause of catalyst deactivation in these materials. Activity loss is primarily due to the physical blockage of active sites and to the clogging of pores. This form of deactivation is reversible. Typically, industrial regeneration of hydrotreating catalysts involves coke burn-off in a high temperature furnace in the presence of a stream of oxidizing gas, usually air or air diluted with nitrogen. In Canada, off-site hydrotreating catalyst regeneration is carried out on a commercial scale by Catalyst Recovery Canada, Medicine Hat, Alberta. Regeneration of hydrotreating catalyst inventories has been undertaken with some success and for certain operations catalyst regeneration and recycling is now an acceptable procedure. However, considerable scope exists for improving industrial catalyst regeneration processes.

1.1 The Nature of Conventional Regeneration

As mentioned, there are several different sources of deactivation of hydrotreating catalysts. The deposition of coke, ash and heavy metals, agglomeration of active metals, sintering of the support material, and poisoning of active sites. Of these sources only sintering of the support, metal deposition and to some degree agglomeration of the active species are irreversible. Ultimately, these factors will limit the number of successful regeneration cycles which may be possible.

Most of the coking of these catalysts appears to take place in the early part of a processing run, with slower deactivation processes taking place over the year or so that the catalyst remains in use (Bogdanor and Rase 1986). The rate of lay-down of coke is dependent on the severity of the catalytic reaction conditions and also on the molecular weight and the nitrogen and oxygen content of the feedstock. N-containing heterocyclic compounds are generally considered to be coke precursors, their strong basic character leading to reaction with Lewis acid

sites on the catalyst surface (Thakur and Thomas 1985). Furimsky (1988) found an enrichment of oxygen in the coke as compared to feedstock, this may indicate the involvement of O-containing ring structures in coke formation. Although most of the coke is formed in the earlier part of the processing run, thermal and chemical processing changes the nature of this coke layer as the run proceeds. Well-aged coke deposits are often quite complex, and are composed of several carbonaceous species (Bogdanor and Rase 1986).

This complex nature of coke deposition may be responsible for the observed variation in the ease in which it is removed by oxidative regeneration. It is felt by many that aged coke which contains less hydrogen may be more graphitic in nature, will be more refractory and will be removed only at temperatures near 500°C (Bogdanor and Rase 1986). The graphitic coke will also tend to be less porous. Thus, the diffusivity of the catalyst will tend to decrease with time as the coke ages (Thakur and Thomas 1985). This aged material is thought to be represented by the component which comes off at the latter stages of burn-off. There are others who believe that this refractory component is not present in the deactivated catalyst but is formed during burn-off (Furimsky and Yoshimura 1988).

There are two fundamentally different processing regimes in which oxidative regeneration may take place. If the reaction temperature is sufficiently low, reaction rates are not affected by mass transport phenomena. In this regime the intrinsic kinetics of the reaction of coke molecules with oxygen will determine the regeneration rate. The rate of coke oxidation is sufficiently slow to allow adequate diffusion of oxygen to all coke molecules in the particle interior. At high temperatures, mass transfer effects are the major influence on the rate of oxidation of coke deposits (Weisz and Goodwin 1963). The extent of mass transfer limitation depends on the oxygen concentration and the reaction rate, but also on the pore structure of the catalyst, the size and geometry of the individual catalyst particles and the packing density of the particles. In hydrotreating catalysts some of these parameters may change markedly as regeneration proceeds.

Since there are both sulphur and carbonaceous compounds on the catalyst surface, the chemical composition of the fouling layer will vary as regeneration

proceeds. Sulphur compounds appear to be removed at low regeneration temperatures and compete for oxygen with the carbonaceous material during burn-off. The physical parameters affecting mass transport may be changing significantly as the composition of the catalytic material changes. It cannot be assumed that physical properties of the catalyst such as density, pore structure and thermal constants remain unchanged as regeneration proceeds. A simple mathematical treatment of conventional regeneration of hydrotreating catalysts is not possible as it is for FCC catalysts (Furimsky and Yoshimura 1988).

Nevertheless, a qualitative understanding may be obtained from the work on FCC catalysts. Weisz (1959) proposed a criterion for the determination of the onset of significant mass transfer phenomena in the oxidative burn-off of coke in individual commercial catalyst particles. In all regeneration processes for which:

$$dN/dt > CD/R^2 \tag{1.1}$$

$$\sim 2.1 \times 10^{-6} \text{ moles/cm}^3 \text{ sec} \tag{1.2}$$

mass transfer effects are predicted to be negligible. Where dN/dt is the rate of coke removal per unit catalyst volume, C is the oxygen concentration, R is the particle radius and D is the effective diffusivity of the catalyst material for O_2 at combustion temperature.

To determine which of these regimes applies to our situation, a calculation based on this criterion may be useful. Using a rough estimate of 5×10^{-3}cm^2/s for the effective diffusivity of the hydrotreating catalyst, an effective radius of 1.5 mm, and an oxygen concentration of 9.5×10^{-6} moles/cm^3 (60% O_2 at 500°C), gives dN/dt =2.1×10^{-6} moles/cm^{3}sec for the limiting combustion rate below which no appreciable mass transport effects will be observed.

Regeneration at rates below this should lead to removal of coke uniformly at all depths in the catalyst particles. Partially regenerated particles should be almost equally regenerated from the outer surface to the core. If the coke is of a similar nature at different radial positions this will indeed be seen (Weisz and Goodwin 1963, Bogdanor and Rase 1986). Regeneration at rates above the limiting rate for mass transport effects will exhibit radially non-uniform regeneration.

Figure 1.2 (after Weisz and Goodwin 1963) shows radial regeneration profiles for regeneration with and without strong mass-transfer limitations.

For regeneration rates much higher than the limit, all of the oxygen which comes into contact with carbonaceous material is instantly consumed. This leads to a shell like progression of the regeneration with a distinct boundary layer in which oxidative regeneration is taking place. Partially regenerated particles will show an outer region of completely regenerated material and an inner region which is still fouled. The rate of burn-off is completely controlled by the rate of diffusion of oxygen into the catalyst and the rate of removal of gaseous products from the particle.

In the mass-transfer limited regime, the rate of burn-off is completely independent of the nature of the fouling deposit. There is a possibility of a mathematical modelling of the regeneration process under these conditions, since the oxygen and regeneration products are diffusing through fully regenerated material, which is physically well characterized.

By TGA it was found that the mass fraction of fouling materials in the spent catalyst is approximately 20%. The laser process involves a total of about 60 dwell times of approximately 1s duration to achieve complete regeneration of a particular spent catalyst extrudate. Thus, the actual time to regenerate is about 60s per extrudate. The combustion rate per unit volume, assuming 100% carbon in the fouling material, is then 1.4×10^{-3} moles/cm^3 s. Substituting reasonable values into the criterion for mass-transfer limitations gives CD/R^2 =7, 21 and 28×10^{-7} moles/cm^3 s for oxygen concentrations of 20, 60 and 80% respectively. Clearly, even if the estimate of D =5×10^{-3} cm^2/s is in error the laser burn-off is proceeding under strong mass-transfer limitations.

In the conventional method the furnace temperature is ramped from room temperature up to 500°C over a period of several hours. Weakly held coke molecules are removed at low temperature, while more refractory material is removed only after prolonged heating at 500°C. The rate of coke removal during conventional regeneration will vary as the process proceeds. Higher rates may be expected at moderate temperatures at the beginning of the regeneration run as weakly held coke molecules and sulphur compounds are oxidized. Again high re-

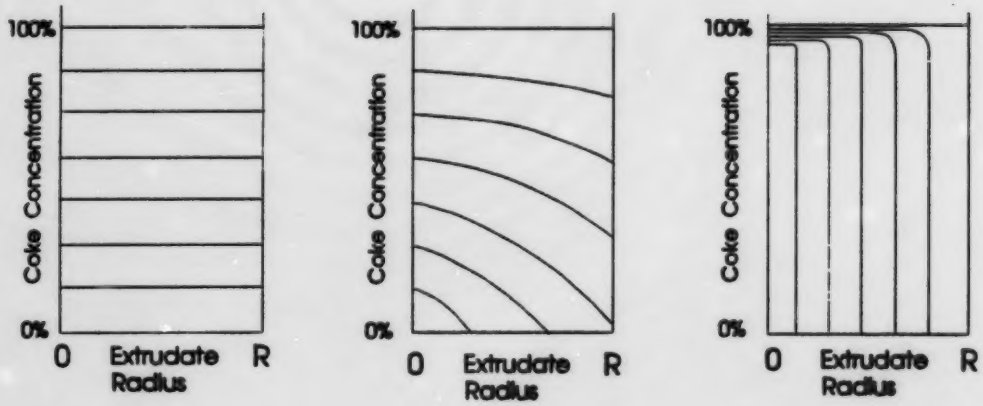


Figure 1.2: Radial regeneration profiles for regeneration progressing in regimes with different mass-transfer limitation.

action rates may occur when the temperature is sufficiently high to remove more refractory coke components. These two regions of higher activity may be seen in TGA plots, and the corresponding gas evolution features have maximum rates at 380 and 450°C (See figure. 3.16)

About 2/3 of the fouling material is removed in heating from 250-400°C with the remainder removed from 400 to 500°C. These temperature regimes have a duration of about 1 and 4 hours respectively, although most material is removed in the early stages of exposure to the higher temperature. Based on this information the maximum rate of reaction during these two phases of conventional regeneration may be estimated.

Thus, the reaction rate per unit volume is approximately 9.3×10^{-6} moles/cm^3 s from 250 to 400°C, and 3.1×10^{-6} moles/cm^3 s from 400 to 500°C. For an oxygen concentration of 20%, these are respectively a factor of 11 and 4.5 above the limits estimated using Weisz's criterion for the onset of mass-transfer effects. These numbers might indicate minimal influence of these effects, but in conventional regeneration gases must diffuse through material which is only partially regenerated. This may reduce the effective diffusivity of the catalyst extrudates. Although no definitive statement may then be made on the importance of mass-transfer effects in the furnace runs, it will be noted that partially regenerated samples from this method showed more radially uniform burn-off than the laser method.

Furimsky and Yoshimura (1988) reviewed recent studies which show that the conventional regeneration of hydrotreating catalysts is indeed very complicated. Among other effects, active and contaminant metal oxides are believed to catalyze coke oxidation. Since the amount of metals in an oxidized state increases as burn-off proceeds, the modelling of the process is complicated. Furimsky also presents evidence that low temperature regeneration in the intrinsic kinetic regime takes place through the production of oxidized intermediates which decompose at higher temperatures to yield gaseous products. The only successful models to date include restrictions such as the lack of metal foulants in the feedstock and a radially uniform deposition of coke within the catalyst particles (Klusacek *et al.* 1985). There are no models available which predict precisely the chemical and

thermal changes occurring within catalyst particles during oxidative regeneration.

1.2 Problems in Conventional Regeneration

The performance of a catalyst is dependent on a complex array of parameters. The regeneration process must reproduce all properties of the original catalyst material. Oxidative regeneration of spent catalysts removes the fouling carbonaceous matter, but may lead to undesirable changes of the catalyst surface. The bulk heating applied during conventional oxidative regeneration can lead to sintering of the support material and agglomeration of the active metals with consequent loss of surface area. The extent of chemical and physical changes occurring during coke burn-off depends on the local surface temperature. Depending on the exothermicity of the oxidation reaction, this temperature may differ significantly from the average bed temperature. Most carbonaceous matter is removed between 250°C and 350°C, but it has been shown that temperatures of up to 500°C may be required to remove unreactive material (Yoshimura and Furimsky 1986). It is at these higher temperatures that most damage is done to the catalyst surface. The duration of exposure at high temperatures must be minimized.

As mentioned, other chemical changes occur during oxidative regeneration of hydrotreating catalysts. Molybdenum and promoter sulphides, formed in situ prior to catalyst use, are converted back to oxides. Surface sulphur is mostly removed as SO_2, but higher local temperatures may lead to the formation of surface sulphates, a permanent contaminant. High local temperatures may also lead to compound formation of active metals and promoters with the support, this may be undesirable.

Prior to a conventional regeneration run, a thermogravimetric analysis is usually performed to determine the temperatures at which coke will be removed. There are generally several distinct temperature regimes over which material is removed. Excessive, or rapid heating during active coke burn-off may cause enhanced sintering due to the presence of water vapour from coke combustion. Again, the exothermic contribution of the combustion process must be considered. Another factor which complicates high temperature regeneration is the

intraparticle migration of active metals at high temperatures, again enhanced by the presence of water vapour. The radial movement of Ni and Mo during thermal processing of hydroprocessing catalysts was noted by Bogdanor and Rase (1986). For these reasons temperatures above 500-550°C are generally avoided in conventional regeneration.

Furimsky (1988) suggests that during the initial stages of regeneration when the most reactive coke species are removed the temperature and O_2 concentration must be reduced. Only by doing so can temperature runaway be avoided with the consequent catalyst damage. For the spent hydrotreating catalysts studied, he found that 350°C and 2% O_2 resulted in an acceptable temperature rise. He also notes that during diffusion controlled burn-off at 20% oxygen concentration or higher, during the final stages of core regeneration, the temperature of the core of a catalyst pellet may exceed the temperature of its exterior. In these situations the catalyst bed temperature may not be an adequate measure of regeneration conditions.

Furimsky and co-workers (Furimsky et al. 1987) examined the possibility of using the Boudouard reaction for regeneration of hydrotreating catalysts. They note that though the equilibrium constant for the reaction of CO_2 with C is several orders of magnitude smaller than that for combustion with O_2, the process is still of interest. The possible advantage of this reaction is that it is endothermic and will not lead to uncontrollable excess heating which is problematic in conventional oxidative regeneration. To achieve complete regeneration using CO_2 as the reactive agent entails heating the catalyst to temperatures as high as 750°C. This would undoubtably lead to undesirable changes in the catalyst, and the Boudouard regeneration process was thus discounted for use with spent hydrotreating catalysts. However, this reaction may still be of interest for use in the initial stages of regeneration or in novel situations such as laser photothermal regeneration. It may be possible to sustain reaction of coke with CO_2 in laser regeneration while minimizing sintering and metals agglomeration, since rapid heating and cooling during the laser method reduces long term exposure to high temperatures.

1.3 Lasers in Catalysis

In previous work with CANMET (Steel and Duley 1989), Powerlasers Inc. investigated the application of laser technology in the catalysis industry. It was discovered that, in this industry, lasers were used only as an analytical tool. Some preliminary investigations into the laser processing of catalytic materials were performed, and several interesting possible commercial applications were discovered. An experimental examination of the laser irradiation of commercially spent Ni/Mo and Co/Mo hydrotreating catalysts proved to be especially interesting.

Exposure of crushed (20-40 mesh) spent commercial catalysts to CO_2 laser radiation in an air stream for periods of the order of one second led to full regeneration. XPS and PIXE analyses showed that the concentrations and oxidation states of the catalytically active metals were equivalent to those of the unused catalyst. The residual amounts of carbon and sulphur in the catalyst were also equivalent to the original unused material. There was no evidence of sulphate formation, a poison of these types of catalysts, which is a sign of local overheating of the catalyst surface. Pore structure analysis of the catalyst material by mercury porosimetry showed that the total pore volume and the pore size distribution were also restored upon irradiation. Although actual use in a HDS reactor is the only definitive test of catalytic activity, these analytical results demonstrate restoration of the major physical and chemical properties of the catalyst particles by the laser method.

Due to these encouraging results the use of CO_2 lasers in the production and regeneration of hydrotreating catalysts was targeted as the application most likely to lead to rapid commercialization. The present project is a more complete investigation of this new laser based method for the regeneration and thermal processing of hydrotreating catalyst materials.

The novel nature of the laser photothermal processing of these materials provides quite different reaction conditions and may lead to distinct advantages. It is clear from the previous work that it is possible to drastically reduce reaction time by using CO_2 laser radiation for thermal processing of coarse powders of catalytic materials. Hydrotreating catalyst particles are typically between 1/32

and 1/4 inch in diameter. Although the previous work is of considerable technical interest, the reaction parameters are not directly applicable to commercial catalyst extrudates. In the processing of commercial catalyst extrudates, mass and heat-transfer to the center of the catalyst particles are a major concern. During laser regeneration of the crushed catalyst, mass and heat-transfer did not substantially limit the processing rate. This is not the case with whole extrudate particles. In the present work, a scale-up of the previously used system allows for the processing of batches of whole catalyst extrudates.

Bench scale reactors for both conventional and laser based processing of catalysts were designed and constructed. A laser irradiation system consisting of a CO_2 laser and beam delivery optics was also designed and included in the laser processing unit. Samples of industrial hydroprocessing catalysts were processed using both systems, with the aim of comparison of the laser based process with the conventional.

A description of the apparatus and processing conditions used to successfully process whole commercial catalyst particles is given in chapter 3 of this work. The results of the investigation of laser regeneration with both the conventional and laser process are discussed in chapter 4. The efficiency of the laser based process is compared with that of conventional regeneration in the electrically heated furnace. The discussion involves both technical and economic aspects of the two processes.

Other possible applications of laser photo-thermal processing of catalyst materials are investigated in chapter 5. Here we look at the possibility of novel effects upon laser processing of catalytic materials. An application which was considered worthy of more detailed study is the laser calcination of catalytic materials in catalyst production. To this end we have impregnated samples of hydrotreating catalysts by both conventional and laser methods. The results of this work are also presented in chapter 5.

Conclusions and recommendations on the future use of lasers in catalyst production and regeneration are given in chapter 6.

Chapter 2

Experimental

Laser photo-thermal processing of commercial catalytic materials is a novel and patented new technology. The laser reactor assembled for this work is the first of its kind, and as such it was designed with intrinsic flexibility. A wide range of processing conditions are possible with the reactor. Laser processing technology introduces many advantages in terms of control over the reaction conditions, but there are significant differences in how processing can be accomplished. Clearly, to take advantage of the unique nature of laser heating, each individual catalyst particle must be uniformly exposed to the laser radiation. Since it has been found that adequate laser processing requires irradiation of all sides of a catalyst extrudate, multiple irradiations are also necessary. For example, between 20 and 60 short exposures are required to completely regenerate coked 1/16 inch extrudate particles.

The laser reactor can process batches of up to 150g of catalyst extrudates. Although strictly a batch reactor, the laser reactor's design is in a manner analogous to a continuous process reactor. The catalyst bed is annular and rotates sequentially through regions where irradiation and agitation take place. Scale-up to continuous processing would simply involve linear translation of the catalyst bed rather than rotation of the annular bed, the process would remain unchanged. This was a major design consideration. The laser reactor was designed to enable a systematic study of laser processing of industrial catalyst particles. Data was collected to aid in the determination of the feasibility for commercial scale-up of

the laser catalyst reactor.

2.1 Apparatus

2.1.1 Laser Source

The laser source consists of two slow axial flow CO_2 lasers giving up to 70 watts each. The output of the tubes impinge on two different areas of catalyst in the regeneration region. The laser tubes are fitted with a closed cycle refrigerated cooling system. Laser radiation is delivered to the reactor in an enclosed optical delivery system. The design of the processing unit does not involve motion of the laser beam, but relies on mixing and rotation of the catalyst bed to ensure adequate exposure. By this design, complex optics and excessive catalyst agitation are avoided.

The laser source was designed and built by Powerlasers. The following outlines the laser source specifications:

Parameter	Specification
Oscillator length	200 cm
Discharge length	~175 cm
dc excitation	50 mA at about 9 kV
	(trigger pulse to 20 kV)
Tube pressure	7-10 torr
	approx. 10% CO_2, 10%N_2, balance He
Flow rate	to 100 changes per minute, ~2.5 l/s
Cooling	3 l/min at 10-20°C
Diameter of optics	2.54 cm
Output coupler	flat R=85%
Rear reflector	concave (5 m center of curvature, R=99.5%)
Beam waist	0.8 cm
Beam diameter	~1cm at 1 m from output coupler
Optical mounts	(~7° rotation ~10 arc second resolution)

Laser Operating Parameters

The lasers were tested and performed fully up to the design specifications. After optimization of the laser operating parameters an output power of 100 W per

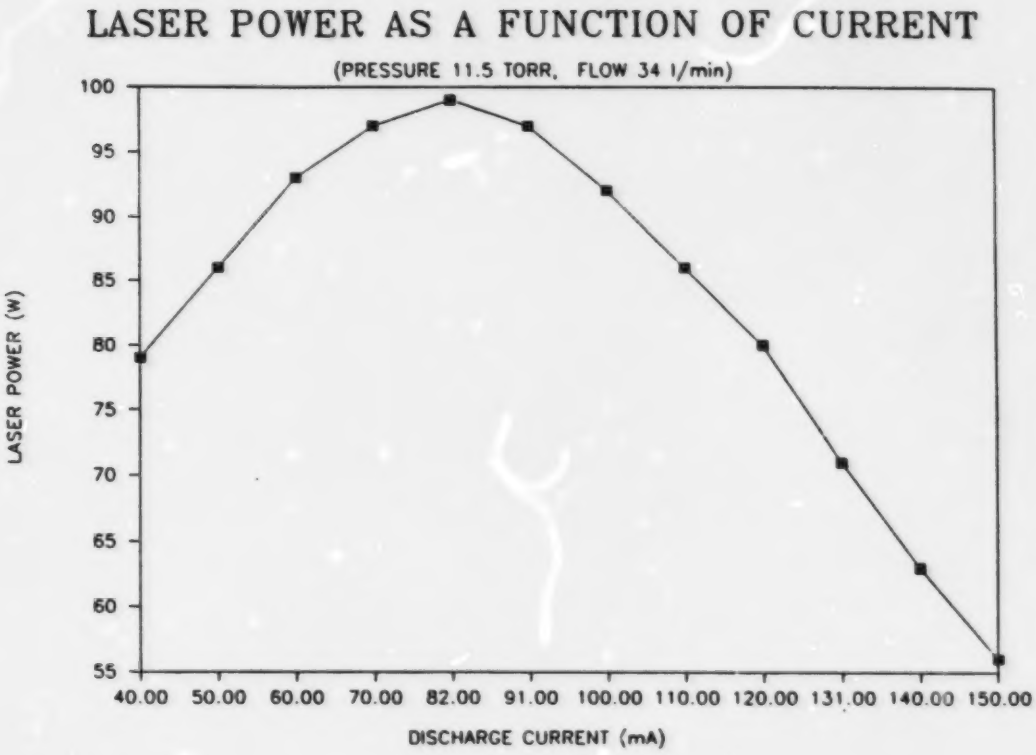


Figure 2.1: Laser power variation as a function of discharge current

tube was obtained. The lasers were operating principally in the TEM_{10} mode, with an output beam approximately 1 cm in diameter at 1 m from the output coupler. The following details the measurements used to determine the optimum operating parameters of the laser tubes.

The dependence of laser power as a function of discharge current is given in figure 2.1. The gas pressure and flow were held constant at 11.5 torr and 34 l/min respectively. The potential across the discharge tube was varied from 9.3 to 11.9 kV to achieve the desired current. The maximum laser power obtained, 99 W in this series of measurements, was found at a current of 82 mA. The voltage applied to the tube for this maximum output was 9.31 kV. Thus the efficiency for the laser was about 13%. A plot showing the variation of laser efficiency and

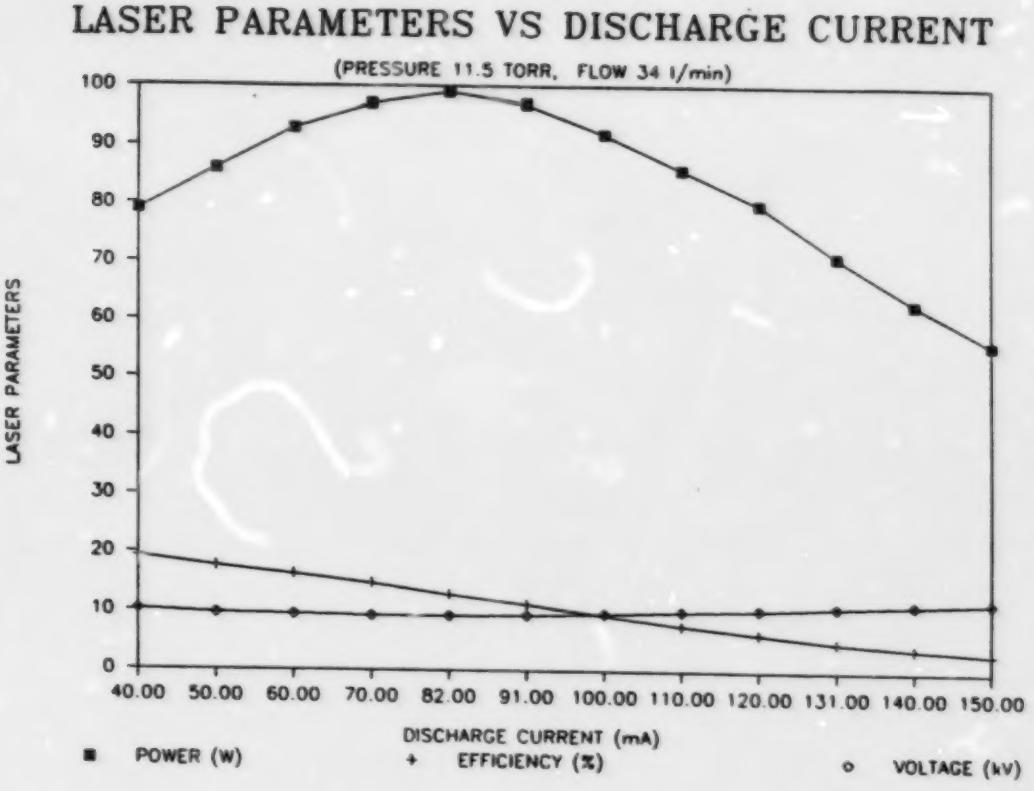


Figure 2.2: Laser efficiency and discharge variations as a function of discharge current.

discharge voltage as a function of discharge current is given in figure 2.2.

We also studied the variation of laser power with flow rate to determine the feasibility of reducing gas flow and so reduce gas consumption. Since the pumping rate was fixed, tube pressure decreased with reduction in gas flow. A plot of maximum laser power versus flow rate under these conditions is given in figure 2.3. It is clear that a flow less than about 34 l/min leads to a reduced laser power. The trend for increased power with increasing flow rate appears to reach a plateau also at 34 l/min. It does not appear that small increases in gas flow will lead to a significant increase in laser power. Sealed lasers with this laser power are available and could be used as a source when gas consumption was to be minimized.

In another series of measurements we reduced the pumping speed, thus in-

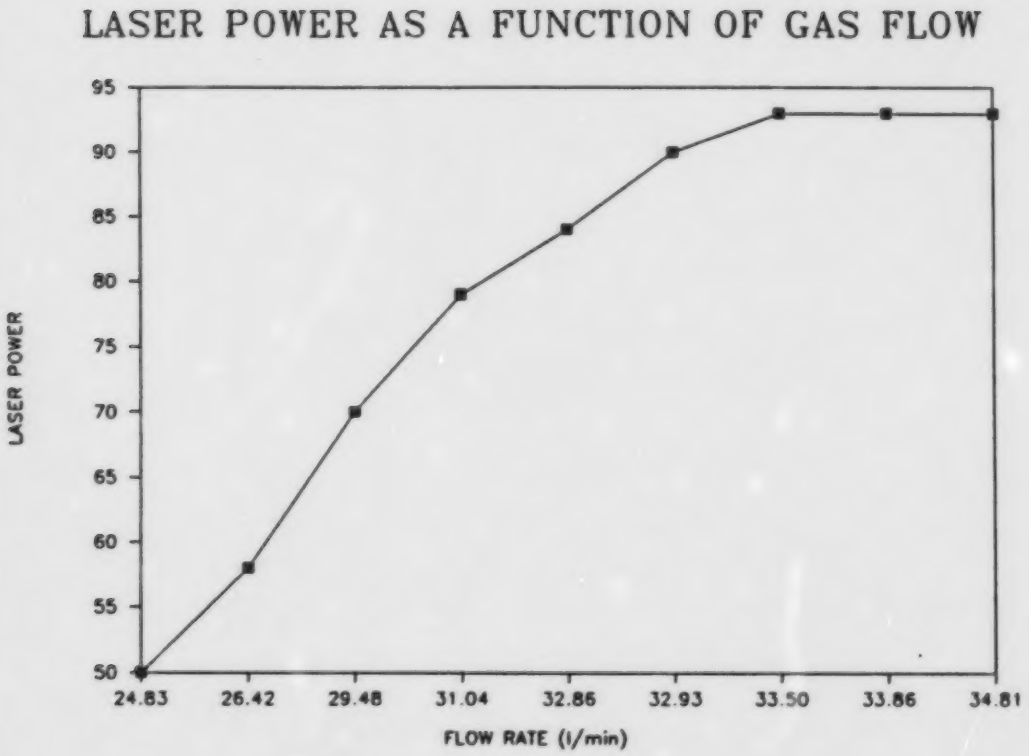


Figure 2.3: Laser power as a function of laser gas flow rate.

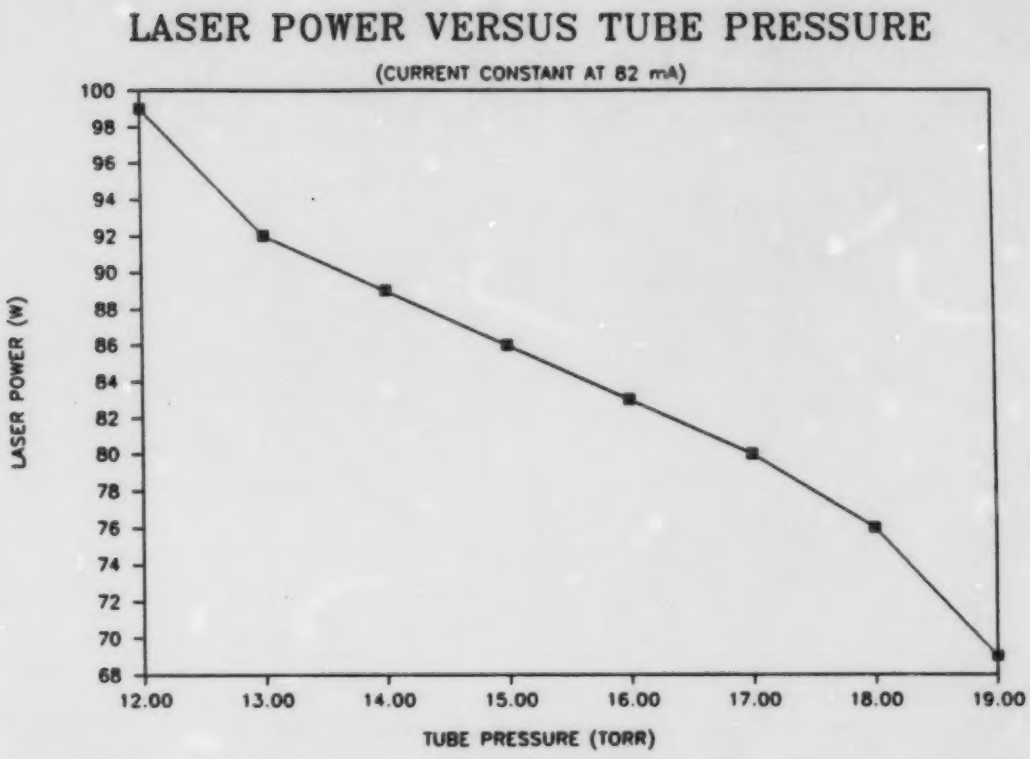


Figure 2.4: Dependence of laser output power on pressure of laser gas in discharge.

creasing the tube pressure, and measured the laser parameters as a function of gas pressure at constant flow rate (constant rate at atmospheric pressure). By fixing the current to that which led to maximum power we hoped to determine the optimum tube pressure. We found with reduced flow that the laser output power decreased steadily with increasing pressure, figure 2.4. It is important to note that the reduced pumping speed led to a reduced flow rate (at tube pressure) in the laser tube, thus increasing the residence time of the gas. In figure 2.5 the variation of other laser parameters with pressure is presented.

In another series of tests the composition of the laser gas mix was varied. The fractions of CO_2 and N_2 were varied independently from 10% to 20%, at a total tube pressure of 11 torr. No significant increase in the laser output power was

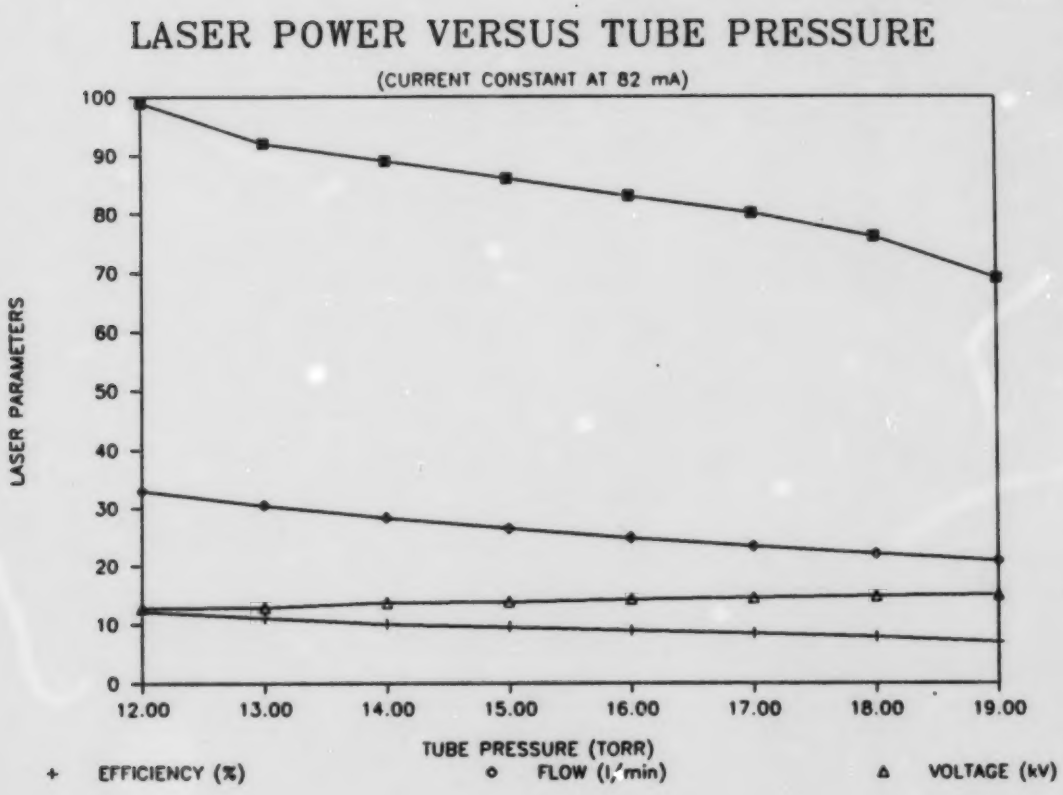


Figure 2.5: Dependence of laser operating parameters on discharge tube pressure.

observed in this study. For all of the results presented in this work, a pre-mixed cylinder of laser gas of composition 10% CO_2, 10% N_2 with balance in He was used.

Based on the preceding measurements, the following are the optimum parameters for the operation of the laser tubes:

Parameter	Optimum Range
Discharge Voltage	9-11 kV
Discharge Current	70-90 mA
Tube Pressure	10-13 torr
Gas Flow (per tube)	greater than 30-40 l/min
Heat Dissipation (per tube)	500-700 W minimum

Laser Pulsing

We have been able to pulse the laser at frequencies from continuous wave (CW) to over 1 kHz. The pulse width is variable to give pulses as short as 100 μs up to 100% duty cycle. Although we have not been able to examine the pulse shape of the laser output, we are confident that we are getting discrete pulses at all available frequencies. The drill holes made by the focused laser radiation as material is passed quickly under the pulsed beam show distinct edges. Furthermore, the duty cycle preset by the laser controls was correctly reproduced on the test plates. The discharge may be ignited and extinguished in less than 64 μs.

The influence of pulsing on the average power output of the lasers was investigated. In one test, the pulse repetition frequency (PRF) was varied, while maintaining the duty cycle at 50%. The following table details the results,

PRF	Power, Tube 1			Power, Tube 2		
(Hz)	CW	Pulsed	Ratio	CW	Pulsed	Ratio
1250	70.6	59.2	0.839	62.3	50.0	0.803
625	67.6	54.2	0.802	60.9	44.6	0.732
156	66.6	48.2	0.724	58.3	38.3	0.657
78.1	67.3	46.1	0.685	56.8	38.1	0.671
19.5	67.8	35.5	0.524	62.2	38.8	0.624

It is evident from above that at constant duty cycle the average power of the laser increases with increasing pulse repetition frequency. When pulsed, the laser

power supplies produce tube voltage profiles which contain the ~20 kV strike voltage followed by the ~9-10 kV voltage which is seen in CW operation. For the duration of the strike voltage there is a greater power input to the discharge, and a consequent increase in the laser power output. This increase is more marked at higher pulse repetition frequencies or smaller duty cycles where for the full duration of the laser pulse the tube voltage is ~20 kV. The following table shows the similar trend in the discharge current.

Frequency	Current Tube 1			Current Tube 2		
(Hz)	CW	Pulsed	Ratio	CW	Pulsed	Ratio
1250	50	32.8	0.656	50	31.8	0.636
625	50	30.9	0.618	50	28.3	0.566
156	50	27.8	0.556	50	24.0	0.480
78	50	29.1	0.582	50	26.0	0.520

2.1.2 Laser Reactor

The core of the laser reactor vessel is a toroidal cavity which holds the catalyst for processing (see figure 2.6). The reactor core is in two pieces, the upper part is attached via pillars to the outer wall of the reactor vessel. These pillars also serve as conduits of gases for agitation and oxidation of the catalyst and provide for the entry of laser radiation. The lower core half is attached to a shaft which passes out of the lower part of the reactor allowing rotation of the catalyst bed.

The rotation of the bed translates the catalyst in a principally static bed past the laser radiation impinging from above. The bed also rotates the particles through an agitation region. The mechanism of the stirring is the vertical flow of gas, tangential to the circular contour of the reactor core. Exhaust ports are located adjacent to the irradiation region and enhance the flow of oxidizing gas in the reaction zone.

In the following description of the construction and functioning of the laser reactor refer to figures 2.6 and 2.7. The numbers of the various parts are as presented in these figures. The laser reactor is of overall circular cylindrical form and its major features are duplicated as can be seen in figure 2.7. The catalyst particles are placed in an annular bed (1), which rotates about its axis (2). This

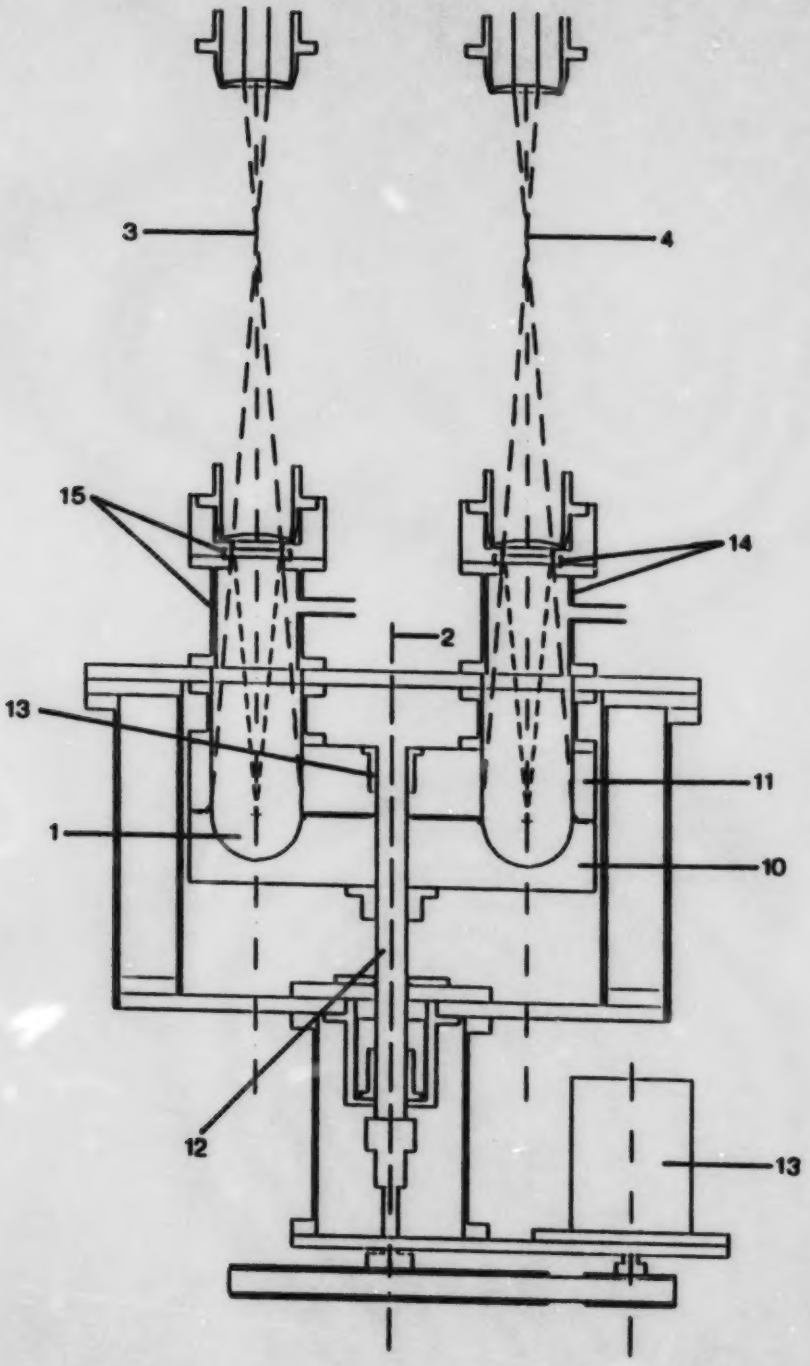


Figure 2.6: Cross sectional schematic drawing of the laser catalyst processing reactor.

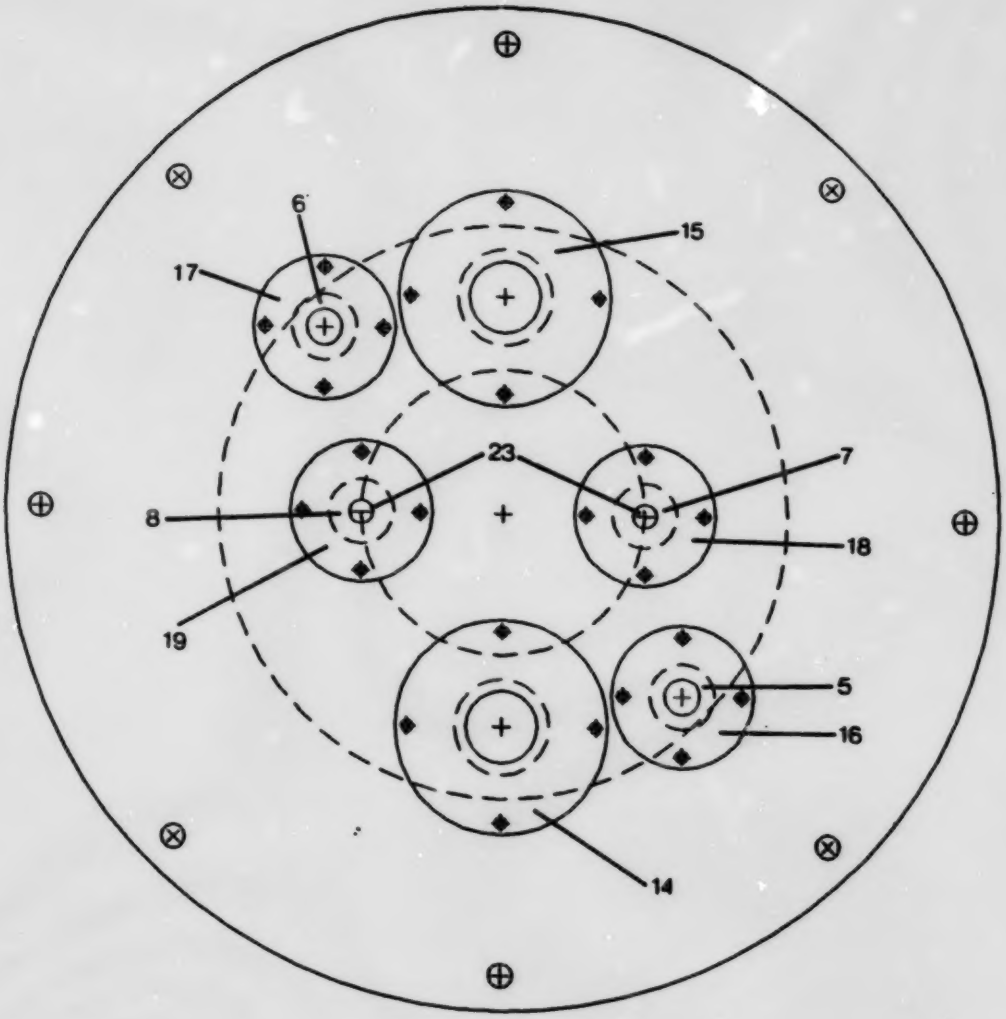


Figure 2.7: Top view schematic drawing of the laser catalyst processing reactor.

bed is fully contained in the interior of the reactor.

The laser reactor is a sealed system, laser radiation and gases enter through airtight ports. The rotation of the bed moves the catalyst particles under the laser radiation (3,4), past an exhaust port (5,6) and into an agitation region where gas flow from inlet nozzles (7,8) leads to stirring of the particles. The gas flow is directed tangential to the contour of the cavity in which the catalyst particles are held. It is this feature, and the smooth curve of the reactor interior which minimizes attrition of the particles upon agitation.

The core of the laser reactor is composed of a lower (10) and upper (11) half. As mentioned above, these two parts fit so as to create the toroidal inner cavity. A shaft (12) is attached to the lower half (11) and passes through the bearing (13) on the upper half (11). This shaft is driven by a motor (13) which serves to rotate the lower half (10), with respect to the upper half, which is fixed via pillars (14-19) to the external walls of the reactor (20). These pillars serve as the ports for access to the catalyst within the reactor core. There are two ports fitted with infra-red transmitting windows (14, 15) which allow the passage of CO_2 laser radiation for processing through holes in the upper core half (2). These pillars are also fitted with gas inlet ports (21) to provide a gas flow to keep the optics (22) clear of processing debris. This same flow may be used to vary the oxygen content of the atmosphere in the irradiation region. Another set of two pillars (16, 17) is used to pass exhaust gases from the processing out of the reactor core. At the inner end of these ports, screens are placed to prevent loss of catalyst particles which may be entrained in the gas flow. A third set of ports (18, 19) is used to provide gas flow to the agitation regions. The nozzles (23) increase the gas velocity, thus enhancing the agitation of the catalyst particles.

The direction of rotation of the catalyst bed (24) is such that the bed rotates sequentially under an irradiation zone (14, 15), an exhaust port (16, 17) and then an agitation zone (18, 19). Since there are two of each type of regions in the reactor, the catalyst is irradiated, and stirred twice per bed revolution.

The results of preliminary processing runs with the laser reactor were used to determine appropriate operating conditions of the laser reactor. Coked samples of Ni-Mo hydrotreating catalysts, were used in several tests of regeneration in

the catalyst reactor. Table 2.1 outlines the runs performed and the information obtained from them during the reactor commissioning.

Table 2.1: Results of preliminary evaluation of laser reactor performance.

Test Run	Parameters Studied	Conclusions and Modifications
1-3	all systems	modify seals, increase gas flow, incomplete regeneration after 1 hr runs
4,5	focusing	get good variation in focal area (0.25-12.5 cm^2) for 75 W CW sharper focus better ~0.5-1.0 cm^2
6,7	bed rotation	slow rotation rates required (0.25-1.25 cm/s)
8	laser power	even at max power (90 W) need elliptical focusing
9	agitation	gas leaks, pressure generated in reactor, large flow required
10	thermocouple	reading lower than expected catalyst temp., maximum temp. reading ~200°C
11	nitrogen only	much reduced regeneration
12	increased duration	after 3 hours regeneration still incomplete must increase severity of reaction
13	increased O_2 conc^n, (60%)	good regeneration of top particles, but agitation incomplete
14	increased O_2 conc^n (80%)	faster regeneration, higher temp. (200°C), achieved regeneration to core

The catalyst material regenerated in these test runs was incompletely processed. Some particles were themselves incompletely regenerated while others had not been exposed to the laser radiation at all. With efficient agitation and with more severe reaction conditions than many of these runs, complete regeneration is possible. An increase in the batch processing time also produces more uniformly processed material.

To give complete stirring and randomization of the catalyst bed, minimum flow rates to the agitation jets must be maintained. Table 2.2 shows flow rates which are appropriate for different batch sizes. In all cases it was ensured that the exhaust screens were clear of all debris so that back- pressure was minimal.

The flow to the optics was maintained at 6.5 l/min for these tests. Throughout all of the regeneration tests performed to date, while the flow to the optics was

Batch Size grams	Minimum Agitation Flow l/min
10	1.8
25	3.0
50	5.6
100	9.5

Table 2.2: Flow rates for various batch sizes

maintained at 3 l/min or greater, there has been little contamination of the IR transmitting windows.

An important experimental parameter for laser catalyst processing is the residence time of individual particles in the laser beam. The manipulation of particle residence time, or dwell time, is primarily achieved through variation of the rate of scanning of the beam over the catalyst bed. The width of the beam is another factor, and this is varied with the radiation intensity. Since variation in batch size leads to variation in focal conditions, the batch size also affects the settings required to select the dwell time. The dwell time quoted is the maximum dwell time. This corresponds to the exposure time of particles located in the center of the catalyst bed where the laser spot has its maximum width.

The irradiated area on the catalyst bed has an elliptical shape. The major axis, l, is transverse to the direction of bed movement and was maintained at 4.0±0.4 cm. The minor axis w, or width of the ellipse, was varied from about 4.0 cm to 0.1 cm to yield intensities from 5 to 150 W/cm^2 respectively. The maximum particle dwell time τ is given by,

$$\tau = w/v$$

where v is the translational velocity of the catalyst bed.

Table 2.3 gives settings appropriate for achieving dwell times of 0.4, 0.8 and 1.6 seconds for a 50 g batch irradiated with three different intensities.

2.1.3 Conventional Reactor

The conventional furnace for calcining and regenerating catalytic materials is shown in schematic cross sectional form in figure 2.8. The retort and all materials

Table 2.3: Experimental parameters which determine particle irradiation dwell times.

Stepper Speed (Hz)	Bed Speed v(cm/s)	Intensity (W/cm^2)	Spot Width w(cm)	Dwell τ(s)
45.1	2.25	35	0.9	0.4
22.6	1.13	35	0.9	0.8
11.3	0.56	35	0.9	1.6
38.1	1.90	50	0.76	0.4
19.1	0.95	50	0.76	0.8
9.52	0.48	50	0.76	1.6
16.0	0.80	100	0.32	0.4
8.0	0.40	100	0.32	0.8
4.0	0.20	100	0.32	1.6

in the reactor core are constructed of 300 series stainless steel. The catalyst is placed within a rotating basket which is inserted within this retort. A gas preheating plenum is separated from the catalyst chamber by a diffuser plate which has laser drilled perforations. To reduce heating of the motor and drive components, the shaft which rotates the catalyst basket passes through a water cooled jacket.

Thermal and Control Design

Heating is provided by a 2.7 kW cylindrical radiative heater spaced 0.75 inches outside of the retort. Insulation is provided by a 3 inch thick blanket of ceramic fibre. An on-off, non-indicating, high-limit temperature controller monitors the output of a thermocouple placed in the space between the heater and the retort. This prevents overheating of the nichrome heater wire and the stainless components. This controller is typically set at 850°C. A more sophisticated proportional-integral-derivative (PID), programmable controller with multiple set-points and digital output is used to provide control of the catalyst temperature using a thermocouple probe located inside the catalyst basket. The PID controller is serially linked to the IBM PC computer.

The control parameters were determined following manufacturers outlines.

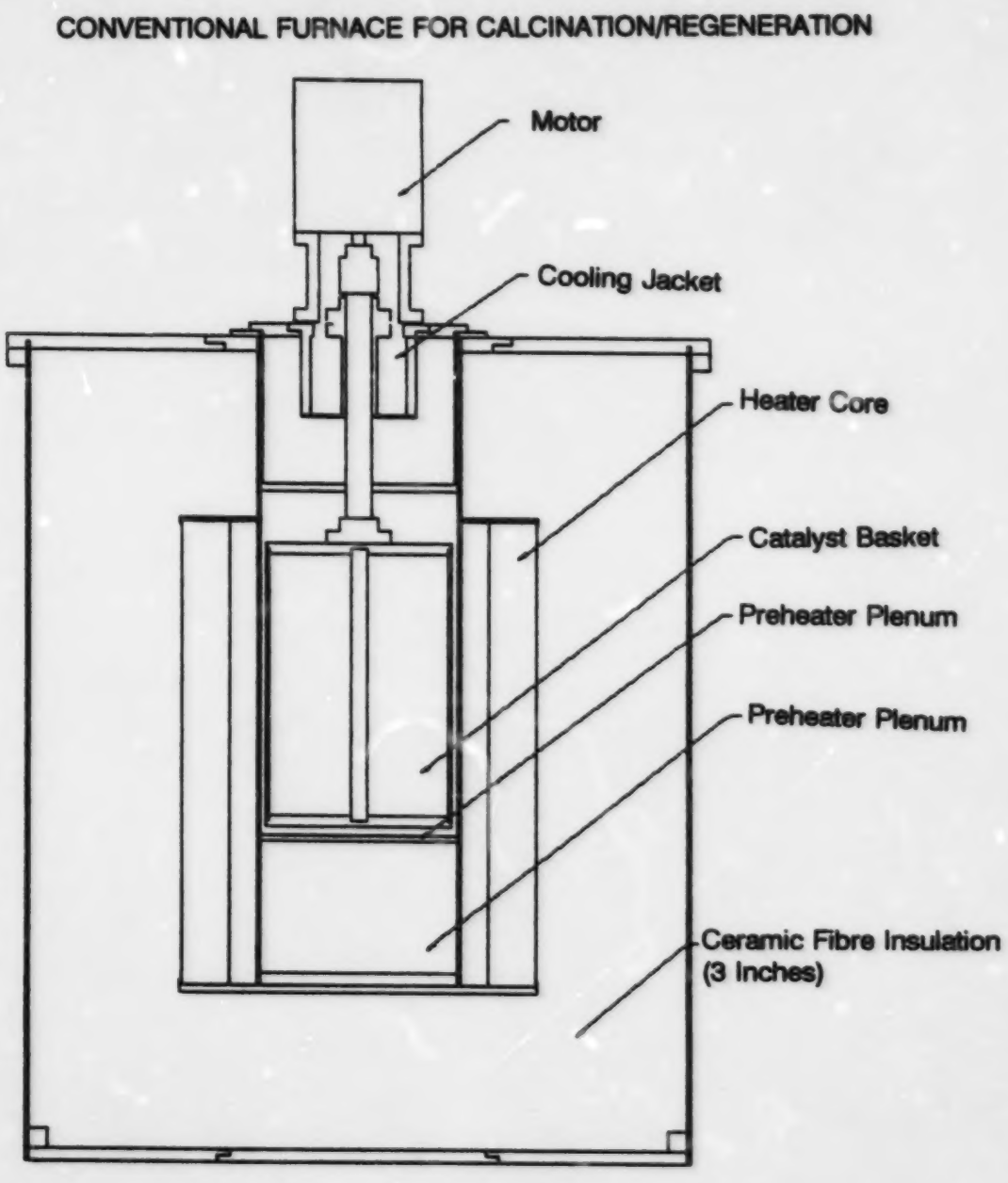


Figure 2.8: Cross-Sectional View of Conventional Furnace

The starting parameters for tuning the controller were taken from the plot presented in figure 2.9. From a cold start full power was applied to the furnace to analyze the system response to a step input. The position of maximum slope was used to obtain T_d, the lumped system time delay, as shown in the figure. Using T_d and the maximum slope, settings for the proportional band width (PB), RESET frequency (integral) and the RATE (derivative) are given by the following:

$$\begin{aligned} \text{PB} &= T_d \times \text{max.slope} \times 100/\text{span (\% of span)} \\ \text{RESET} &= 0.4/T_d \text{ (resets/minute)} \\ \text{RATE} &= 0.4 \times T_d \text{ (minutes)} \end{aligned}$$

Following some adjustments to the parameters to account for observed overshoot, the parameter set used is:

$$\begin{aligned} \text{PB} &= 80\% \\ \text{RESET} &= 0.01 \text{ resets/minute} \\ \text{RATE} &= 5.00 \text{ minutes} \end{aligned}$$

The following are the calculations which were used in the thermal design of the conventional reactor. The major sources of heat loss in the furnace and the amounts lost per hour are shown in table 2.4.

Heat Losses In Furnace, 750°C at Core			
Loss Pathway	Parameter	Loss (BTU/Hr)	Loss (W)
Gas Flow	12 exchanges/min	540	160
Retort Walls	0.03" walls	1200	343
Shaft	0.03"walls	64	20
Insulation	2.5" thick	1380	400
Total Losses	—	3184	925

Table 2.4: Sources of heat loss and amounts for the conventional furnace

Based on heat flow calculations, the temperature of the furnace walls and the conductive losses are shown in table 2.5

In practice, the furnace may readily be used to achieve processing temperatures from less than 100°C up to 800°C. With a full basket of catalytic material the heating time constant is quite large, of the order of 2 hours. Temperature changes must take place over times of this magnitude to avoid overshoot in the processing temperature.

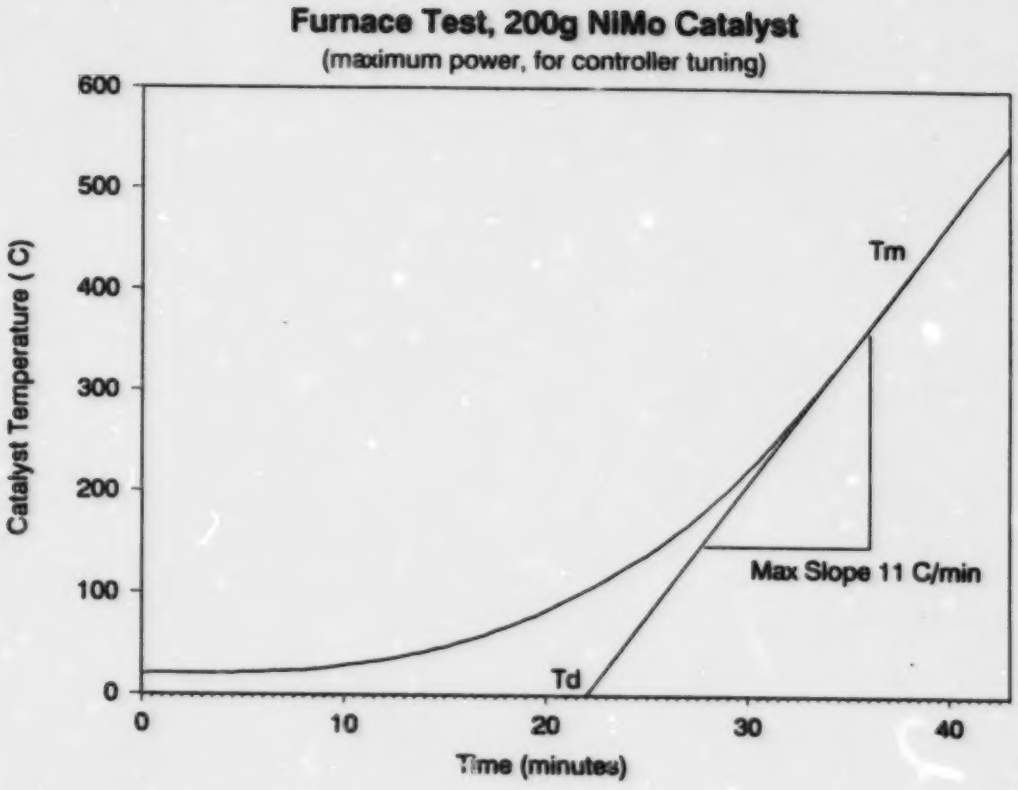


Figure 2.9: Plot showing temperature rise in furnace core, during full power test. Note the relevant parameters deduced from the plot.

Retort Temp	Outer Wall Temp	Total Heat Loss (btu/hr)
°C	° C	
480	46	198
540	50	243
595	55	330
650	60	345
700	67	408

Table 2.5: Heat flow calculations for the conventional reactor

2.1.4 Process Control and Data Collection

The process controller is an IBM PC compatible computer fitted with a commercial data acquisition and control card. This system allows for the efficient collection of processing data, and facilitates the control of processing variables. Inputs to the controller are the temperature of the catalyst bed in the regeneration region (by thermocouple) and the laser power (by thermopile). The significant processing parameters which are determined by the laser are

Parameter	Controlled By	Influences
laser intensity	laser power and focusing	temperature, reaction rate
particle residence time	rotation rate	depth of heat penetration
total fluence	laser power, total processing time	cost of process

For optimum processing, the laser intensity and the residence time may need to be varied during the course of a batch regeneration. These may readily be controlled by varying the laser power and the rotation rate of the bed during processing. The operating temperature of regeneration zone must be carefully maintained to prevent catalyst damage by temperature runaway. Although these possibilities were not investigated, they may be accomplished with very simple modifications to the control software.

The following were design criteria in the process control and data acquisition:

- Full laser control is available from the main rack. Gas flow, current and beam on controls will all be available to operate the laser without the remote data acquisition PC computer being active.
- The remote system is serially linked to the analog-to-digital cards, TTL I/O cards and the stepper control card installed on an ALPHA bus, within the main control rack.
- From the remote host the user may select a pre-composed control program and initiate a serial transfer. This control program will initiate temperature sampling, toggling of beam on/off, and display and update parameters on the display screen. Temperature histories are stored on the host hard drive, available for display and analysis when desired.
- In the case of catalyst overheating or other fault conditions, the controlling program may terminate power to the faulty system and display appropriate warnings.

Drawings of the electronics for control and data acquisition are given in appendix A. In appendix B, the source code for the control program is included along with a flowchart of the menus used for on screen selection of process and data acquisition parameters.

2.2 Analysis of Catalytic Materials

The processed materials were characterized using several different analytical techniques to determine the effects of laser treatment. Both chemical and physical properties were examined.

2.2.1 Physical Characterization

During the commissioning of the laser reactor the quality of most of the regenerated material was judged as inferior to that produced by conventional methods.

There was difficulty in obtaining core regeneration, while splintering and loss of structural strength was noted in extrudates from many regeneration runs. Upon consultation with the scientific authority, the emphasis of analysis was changed so as to be used to determine the acceptable operating regime of the reactor, rather than the determination of the fine details of the chemical and physical make-up of the regenerated material.

Crush Strength Determination

An apparatus was constructed to measure the crush strength of individual catalyst particles. Individual catalyst extrudates are held between two horizontal, parallel plates. The lower plate is fixed and has a shallow well to locate its centre and contain the crushed material after completion of the test. The upper plate is fitted with a mechanism which allows for the application of a continuously varying stress to material held between the plates. A strain gauge bearing on the centre of the upper plate measures the deformation of the particles as a function of applied stress.

The experimental error in measurement of the applied force required to crush the particles is difficult to ascertain since no two individual catalyst pellets are identical in either dimension or strength. The determination of the stress involved an estimation of the effective surface area which is bearing the measured force. In the progress of a strength measurement several discontinuities in the measured strain were usually detected prior to catastrophic crushing of the particle. Although these minor discontinuities in strain came at different stress values in each sample, the point of catastrophic failure was more consistent. Within a particular batch of extrudates, the force measurements upon catastrophic failure agreed to within about 20%. Values for crush strength were taken as the average of three or more measurements of particles from a batch.

The determination of the actual stress which the particles can sustain is somewhat difficult to determine. The surface area of the catalyst touching the plates varies considerably during the course of a measurement. The small jumps in strain during the ramping of stress are due to cracking and superficial crushing of

the extrudate. These effects introduce greater uncertainty in estimation of absolute values for maximum stress, but relative values are reliable within the errors mentioned above. To provide a reasonable estimate of the true maximum stress at failure, an area equivalent to the full length and half the width of the extrudate was used. The length of each catalyst particle was measured with a precision of 5%, but since the ends were not perfectly square, some visual estimation was required.

Scanning Electron Microscopy (SEM)

Scanning electron micrographs were obtained using a Hitachi model S520 SEM with a primary electron beam energy of 25 keV. The ultimate resolution of this instrument is near 40 Å, but the effective resolution was typically much less. A vapour deposited film of Au-Pd approximately 150 Å thick was applied to avoid sample charging. Samples of catalytic materials were examined by this technique to detect surface microcracking and other gross defects due to thermal processing. Fine pore structures and active metal microcrystals are not visible in the micrographs, but porosity of the order of 100 Å is discernable.

Visual Percent Regeneration

The degree of regeneration of partially regenerated materials was estimated visually using a low power optical microscope. An estimate of volume unregenerated was taken from visual appearance of the cross-section of an extrudate broken transverse in the middle. The width of the unregenerated inner region was measured, and the ratio of the corresponding area to the full cross-section was taken as the fraction not regenerated. There are several different possible sources of error in this measurement. The boundary between the coked region and the clean region is often indistinct, so the dimensions of the coked area must be estimated. Increased exposure of the ends of individual extrudates to laser radiation, and enhanced mass transfer, will decrease the amount of unregenerated material in these portions. This was not taken into account in the estimation.

2.2.2 Chemical Characterization

Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra were recorded in reflectance using a Nicolet 20 SX FTIR spectrometer with a diffuse reflectance attachment. The samples were ground and pressed into a flat layer on the sample post. Spectra were recorded in the wavelength range from 400 to 4000 wavenumbers. The resolution of the spectrometer was set to 0.5 wavenumbers. These spectra were primarily used to detect the presence of characteristic absorption features due to vibrational transitions of compounds known to be present in the catalyst samples.

Proton Induced X-ray Emission Spectroscopy (PIXE)

The PIXE analysis was performed by Element Analysis Corporation in Tallahassee, Florida. The catalyst samples were crushed to a powder finer than 200 mesh and are pelletized prior to being placed in the sample holder. The instrument employed is composed of a General Ionex 4 MeV Tandem Accelerator with a dual plasmatron source, a dual quadrupole focusing lens and a 30 mm^2 Si(Li) detector. The energy resolution of the instrument is 150 eV, and the beam intensity was set for a count rate of 75 s^{-1}. The experimental errors in element concentration vary with element sampled, and with the concentration.æ

2.3 Experimental Design

We have undertaken a systematic study of laser regeneration with the laser reactor. Using Taguchi methods we designed a parametric study of the laser regeneration process. This study was used to systematically determine the optimum parameter set for the laser process. The important parameters which were included are those relating to the amount of thermal energy provided, the rate reaction and the rate of removal of reaction products.

Parameters relating to the thermal energy available are the laser energy input (intensity and dwell time) and the oxygen concentration (exothermic heat contribution). The rate of the reaction is determined by the catalyst temperature, the nature of the carbonaceous deposit and the oxygen supply to the reaction site. The latter depends on the oxygen concentration, gas flow and packing density. Parameters relating to the rate of removal of reaction products are gas flow, dwell time, and packing density.

The six relevant processing parameters which were considered as variables are:

- radiation intensity
- dwell time
- oxygen concentration
- catalyst temperature
- catalyst particle packing density

The above set of variables over-specifies the parameter set for the regeneration tests. The first four parameters in this list are not independent. Only three of the first four parameters are required to adequately characterize the reaction conditions for regeneration if all others are held constant. To use temperature as a factor would involve independent fixing of catalyst temperature while holding other process parameters constant. This is not possible without having an iterative approach to obtaining each desired temperature, a laborious process. For

this reason. temperature was used as a critical response and not as a factor in the experimental array.

Two important experimental parameters which were fixed in this study are the total energy deposited per unit mass and the total gas flow rate. A set of pre-trial laser regeneration runs (PT1 - PT7) were performed to determine the appropriate levels for the Taguchi factors. A 120 minute batch time was found to fully regenerate a 50 g batch of catalyst at laser power of 55 W (samples PT3 and PT6), so the mass fluence chosen was that corresponding to these runs. The total laser power in these runs was 120 W, total processing time of 7200s gives 864 kJ per batch or 17.3 kJ/g. This value was used in all of the runs. The lowest oxygen concentration used during laser burn-off was when using un-enriched air. With 15 l/min air flow when processing a 50 g batch, there is an excess of at least 50 times the amount of oxygen necessary for combustion. This was considered adequate, since the oxygen concentration would be insignificantly changed in passage through the reactor.

An L_9 Taguchi array was used, as shown in table 2.6, with the following factors: A=radiation intensity, B=dwell time, C=packing density and D=oxygen content. Gas flow and mass-fluence were held constant, while catalyst temperature, crush strength and core regeneration are taken as the initial response. Based on the pre-trial experimental experience levels (1, 2 and 3) for the factors were chosen to maintain catalyst temperature within an acceptable range (a minimum amount of visible incandescence). The table 2.7 shows the resultant physical characteristics of the pre-trial runs.

It is observed that intensities in excess of 100 W/cm^2 may lead to excessive cracking and even explosive splintering of catalyst extrudates. Crush strength of material processed under high intensity radiation is reduced. There is also an increase in attrition, due to splintering and fine dust production. Due to the bright blue or yellow colouration, the dust appears to be rich in active metals (Co/Mo or Ni/Mo). This is obviously undesirable.

Intensities less than 25 W/cm^2 have been shown to produce only superficial regeneration. Greater intensities are required to produce adequate core regeneration.

	FACTORS			
TRIALS	A	B	C	D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

Table 2.6: L_9 Taguchi orthogonal array. A=radiation intensity, B=dwell time, C=packing density, D=oxygen concentration, 1=low, 2=medium, 3=high.

	Regeneration Conditions				Physical Characterization	
Sample ID	Mass (g)	I (W/cm^2)	Dwell (s)	$[O_2]$ (%)	Colour	Crush Strength (N)
PT1	10	100	0.4	60	red-grey	64
PT2	10	50	0.4	60	brown-grey	107
PT3	50	100	1.0	60	green-grey	74
PT4	50	50	0.8	60	brown	127
PT5	50	50	1.2	80	red-brown	>127
PT6	50	50	1.5	80	grey-yellow	103
PT7	50	35	2.4	80	brown-yellow	98
KJN	unused Ketjen Ni/Mo				green-yellow	40

Table 2.7: Physical characterization of pre-trial regeneration samples.

The use of pure oxygen for regeneration leads to a very rapid temperature rise immediately upon initiation of processing. The temperature rise is accompanied by a very bright glow from the irradiation region. This incandescence is sustained for a period after laser shut-down. The self sustaining coke combustion leads to an uncontrollable temperature rise, and likely causes loss of catalytic activity through many of the mechanisms discussed earlier. A regeneration run was not completed when using pure oxygen. Oxygen concentrations from closed to 0 to 80% have been used in regneration. Core regeneration was obtained under atmospheres containing 20 to 80% O_2.

Dwell times of less than 0.2s appear unable to provide for bulk regeneration of the catalyst extrudates at acceptable laser intensities. Dwell times much larger than 2s lead to excessive surface temperatures for all but minimal radiation intensities.

Based on the findings of the preliminary regeneration runs the following were chosen as the levels of the factors in the matrix study of the laser process:

Matrix Factor	Low	Med	High
Laser Intensity (W/cm^2)	35	50	100
Oxygen Concentration (%)	20	60	80
Packing Density (batch size, g)	10	25	50
Dwell Time (s)	0.4	0.8	1.6

Chapter 3

Laser Regeneration of Hydrotreating Catalysts

The laser regeneration process differs significantly from conventional thermal processes in several areas. During the laser regeneration process, laser radiation is applied directly to the catalyst particles. The energy used is absorbed by both the coke layer and the catalyst itself. The bulk temperature of the catalyst bed rarely exceeds 250°C during regeneration. This stands in contrast to conventional regeneration which requires the heating of furnace components to processing temperature prior to initiation of oxidative burn-off. The laser energy required to initiate and sustain coke burn-off is provided only where needed, there is little excess heating of reactor components.

During conventional processing, the temperature of each individual catalyst particle in the bed is approximately equal to the overall temperature in the furnace. This temperature, and possibly the oxygen concentration, are increased slowly to prevent thermal run-away due to the exothermicity of the combustion reaction. This type of processing necessitates exposure of the catalyst to high temperatures for an extended period of time. Sintering may occur if there is insufficient gas flow through the catalyst bed during regeneration. If not quickly removed, water vapour released during combustion will enhance sintering, intra-particle metal migration and other deleterious effects. The laser regeneration process involves the exposure of individual particles to high temperatures for

very short periods of time. As mentioned above, the ambient bed temperature will be much lower than that necessary to cause sintering.

The amount of oxygen present and the laser intensity are important parameters for laser regeneration. Some sample runs demonstrating their effect on catalyst temperature during regeneration are presented in figure 3.1. The temperature recorded during the regeneration runs is that of the catalyst bed about 1cm from the irradiation region. This corresponds to about 1.5 seconds after exposure to the laser beam in the irradiation region. Although the temperature measured is not the surface temperature of the catalyst under irradiation, it does provide a useful record of the catalyst processing. The laser power, the focusing conditions, the residence time of particles in the laser beam and the gas flow were similar for these runs except where noted. The relevant parameters are:

- laser power 60-70 W
- irradiation intensity 50-100 W/cm^2
- agitation gas nitrogen, flow 30 l/min
- oxidation gas air, flow 7.5-10 l/min
- particle translation speed 0.5 cm/s

Several interesting observations may be made from the data presented here. Many regeneration runs show a sharp initial increase in temperature, peaking at 140-180°C followed by a slight reduction and levelling. It was found that runs which exhibit this peak produced more fully regenerated catalyst than those that didn't. This feature is associated with regeneration under more severe conditions. This trend of a sharp initial rise and peak in the temperature profile is probably due to lightly held, easily oxidized coke molecules. So that this temperature peak is caused by heat released during the oxidation of this component of the coke. Heat is released more slowly from the oxidation of more refractory coke, and this leads to a slight elevation in the reactor temperature, whose contribution decreases until regeneration is complete.

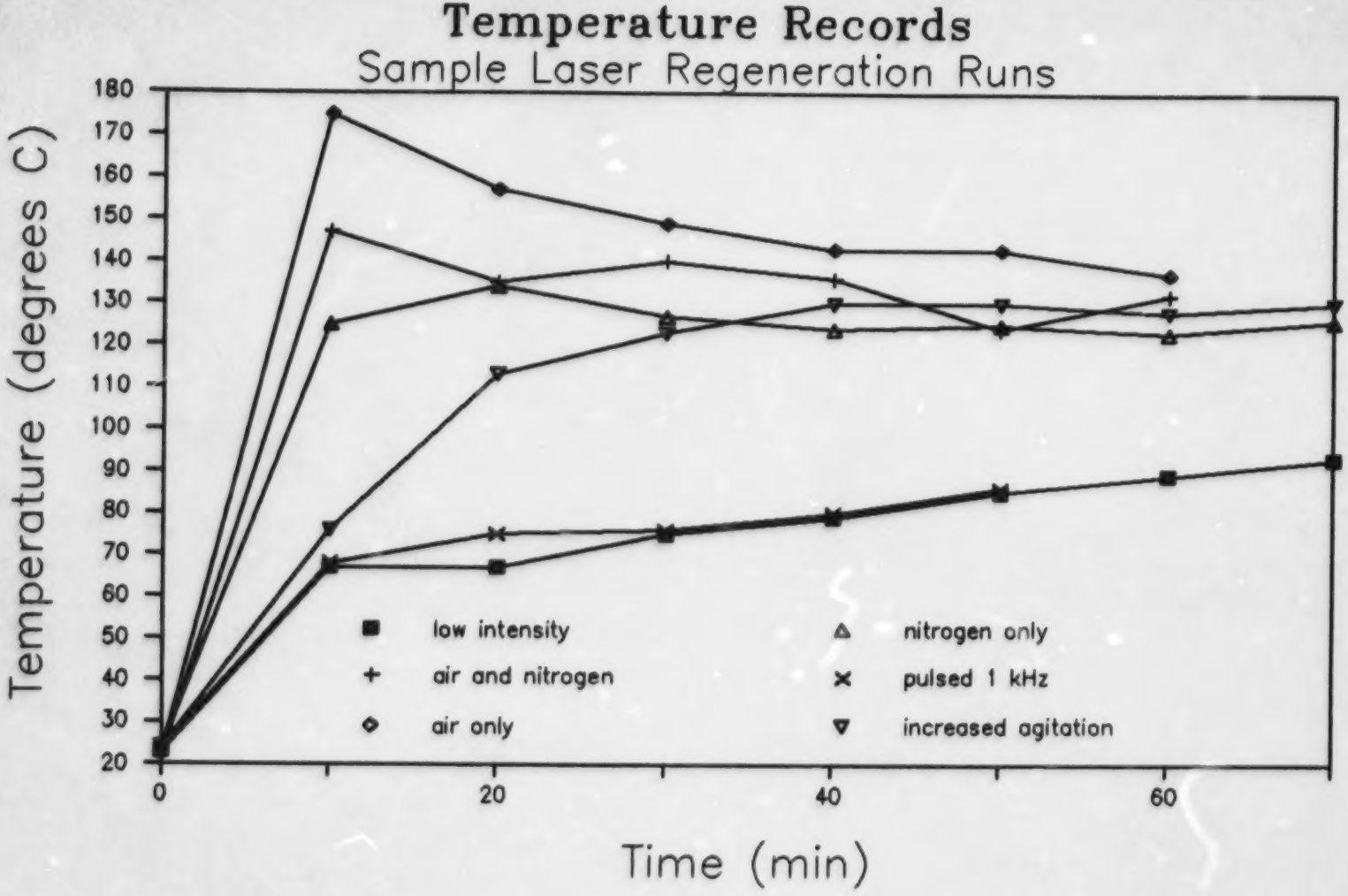


Figure 3.1: Sample laser regeneration runs, I=50-100 W/cm^2, τ=1-2 s, gas flow ~40 l/min total.

There appears to be a threshold in oxidation severity below which there is little contribution from the oxidation reaction to the catalyst temperature. As is evident in figure 3.1, regeneration with low intensity ($\leq$15W/cm^2), low average power (pulsing), reduced residence time (increased agitation), and low oxygen concentration all lead to temperature records with slow initial temperature rise and no peak. These processing conditions also tend to yield less completely regenerated materials.

The low intensity run and the pulsed run (figure 3.1) have very similar temperature records. The pulsing frequency was such that the irradiation period was much smaller than the thermal diffusion time through the width of the catalyst particle (approximately 0.1s). Excluding thermal shock effects, which do not appear to be a significant positive factor, the laser pulsing has the same effect as does a reduction in laser intensity. For laser pulsing to be an effective parameter, we must match the duration of a pulse to the time required for the given laser intensity to heat a catalyst particle to regeneration temperature. At the same time overheating of the skin of the catalyst particle must be minimized.

The run with increased agitation shown in figure 3.1 also lacks the sharp initial temperature rise to a peak. Increased agitation has been observed to sustain particle movement in the irradiation zone. This would result in a reduced residence time of the catalyst particles in the laser radiation. The reduced exposure time results in a reduction in bulk temperature and a smaller increase in catalyst temperature due to oxidation.

It appears that a higher oxygen concentration gives a larger initial rate of temperature increase, larger initial temperature peak, and higher overall temperature resulting in faster regeneration. The absence of oxygen in the gas flow does not completely eliminate coke removal, but the initial rate of temperature increase is dramatically reduced. In this case the temperature of the catalyst approaches that for oxidative regeneration after about 30 minutes of processing.

In the preliminary studies it was noted that there was a significant amount of attrition which seemed to increase with the irradiation intensity. Deposition of a fine powder over the interior of the reactor was noted at very high intensities (>100 W/cm^2). This powder is grey-green from Ni/Mo samples and blue from

Co/Mo samples. In addition to this fine powder the larger catalyst pieces were found broken off the extrudates. The mechanism of the cracking and splintering observed is possibly uneven thermal expansion or rapid production and release of gases within the catalyst particles. It was felt that some residual liquid hydrocarbon or tarry residue may be responsible for explosive release, and trapping of gases. This material could block catalyst pores thus inhibiting the removal of gases. This would not only be undesirable because of the increased attrition, but the rapid exothermic reaction of the liquid hydrocarbons may lead to excessive catalyst temperatures.

A study of the effect of extracting the spent catalyst with hexane and toluene prior to regeneration was performed. It was hoped that this process would remove liquid hydrocarbons and tarry residues, thus opening up the pore structure and facilitating burn-off of coke deep in the catalyst particle. After Soxhlet extraction for several hours with both hexane and toluene, there was little evidence of residue in the solvent. After drying, materials cleaned in this manner were regenerated in the laser reactor. There was no difference apparent in regeneration, and this process did not solve the cracking or splintering problem which was observed.

This finding is in contrast to the work of Furimsky (1988), who found that solvent extraction of spent hydrotreating catalyst material made a marked difference in regeneration. He found that the rate of sulphide removal was increased, and the reactivity of remaining coke molecules was reduced. The change which took place upon extraction was the removal of weakly held very reactive coke molecules. Removal of this material led to the opening of catalyst pores thus allowing oxygen to penetrate to the sulphided layers, facilitating its oxidation.

It may be that the spent catalyst studied in this work was well extracted prior to shut-down of the commercial reactor. The cracking experienced when regenerating with higher laser intensities must be due to rapid coke gasification or to uneven thermal expansion of particles. It has been observed when regenerating under severe conditions that some regenerated extrudates take on a bent or curved appearance. This also may be indicative of uneven expansion during irradiation.

3.1 Catalyst Regeneration Study

As discussed in section 2.3, the matrix study involved nine experimental trials with different process parameters. The records of catalyst bed temperature during these regeneration runs are presented in figures 3.2 to 3.10. This temperature is not equivalent to the temperature of the catalyst particles under irradiation, but it does give an indication of the severity of the reaction conditions. The thermocouple was located about 1 cm from the edge of the irradiation region, so that particles rotate by immediately after processing. The depth of the thermocouple was varied with the batch size so that the temperature measurement corresponds to that of recently irradiated particles. Should there be self sustained coke combustion outside of the irradiation region, this would show up as a significant increase of the observed bed temperature. This is so because heat from sustained burn-off would be released much closer to the thermocouple probe, so particles would have less time to cool.

The process variables were chosen such that the most severe conditions led to a dull orange incandescence of the catalyst particles under irradiation. There is a random variation in bed height of about 0.5 cm during processing. This in turn leads to some variability in the laser intensity. This is due to the method of beam focusing, which causes the radiation to be converging in one dimension at the bed surface. The variation in intensity causes some particles to be exposed to slightly higher or lower processing temperatures. The only evidence of this depth variation is in some periodic variation in the bed temperature when the bed has been unevenly distributed about the reactor core (see figure 3.6). Presumably this is due not to differences in catalyst temperature but to the thermal contact of the thermocouple probe with the top of the catalyst bed.

The temperature profiles vary in shape with the severity of the burn-off conditions. The most severe reaction conditions produce the sharp initial temperature peak, and higher overall bed temperatures (figures 3.4, 3.5, 3.8 and 3.9). Low oxygen concentrations (figures 3.3, 3.6 and 3.10) and low intensities (figure 3.2) led to a more gradual increase in bed temperature. Trials 3, 4 and 8, which all led to significant regeneration of the spent catalyst, had the initial peak in temper-

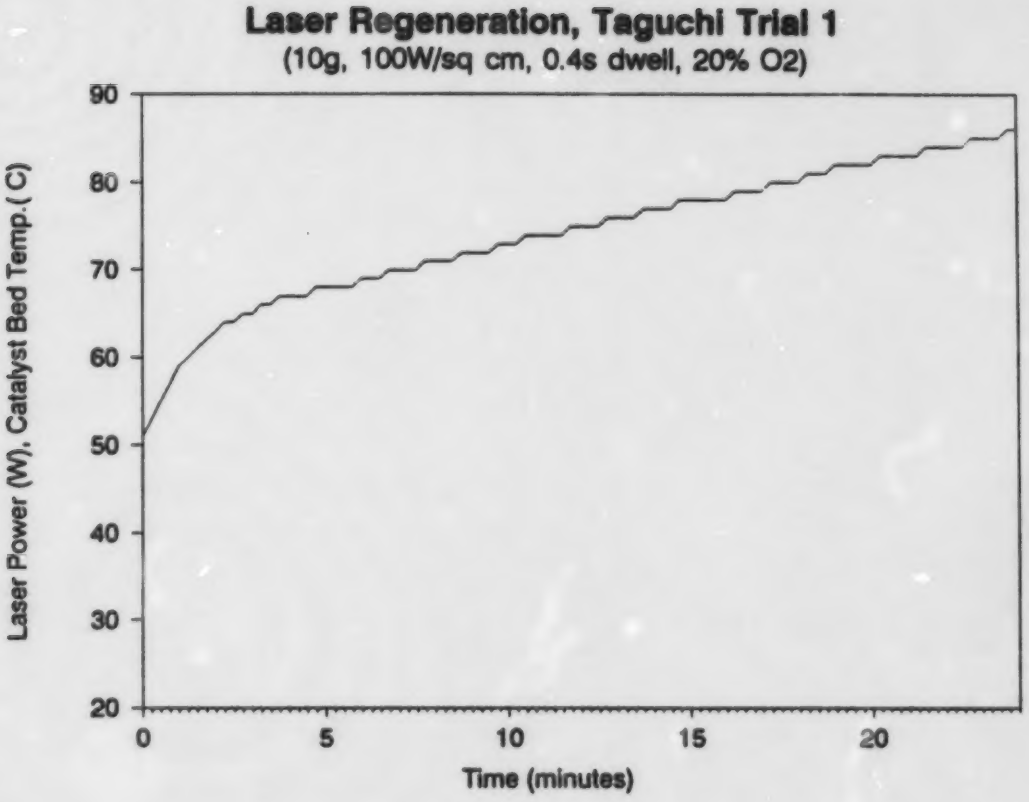


Figure 3.2: Catalyst bed temperature record during the laser regeneration of spent Shell 424 NiMo hydrotreating catalyst, matrix trial 1.

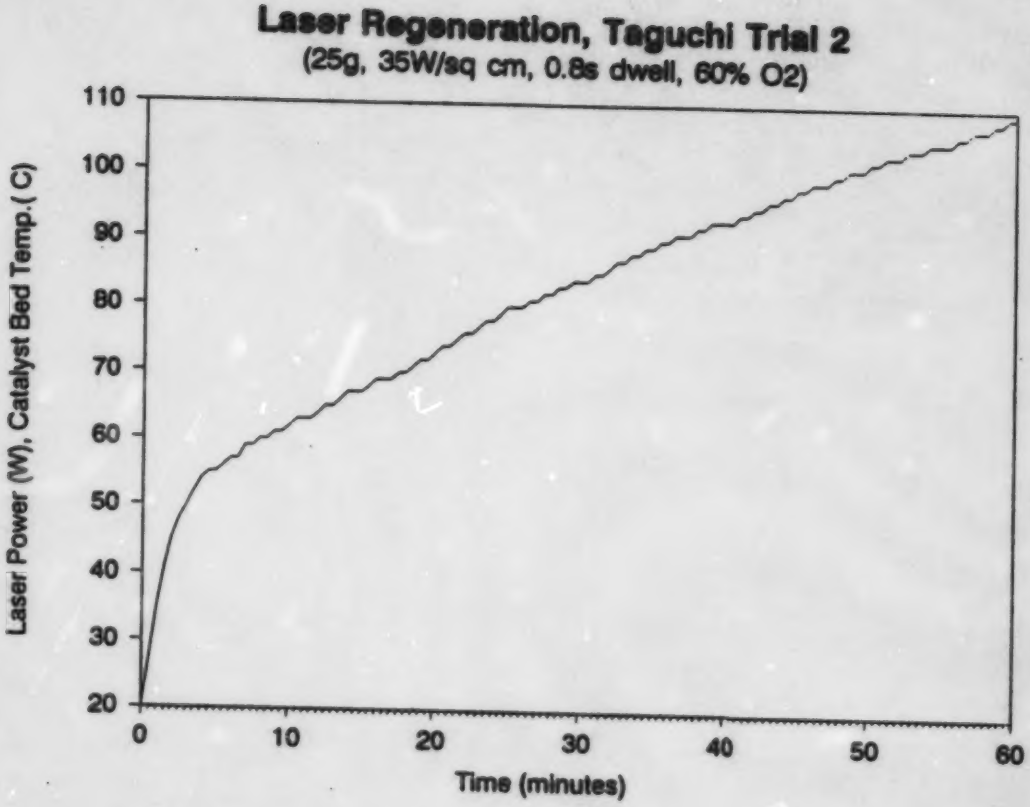


Figure 3.3: Catalyst bed temperature record during the laser regeneration of spent Shell 424 NiMo hydrotreating catalyst, matrix trial 2.

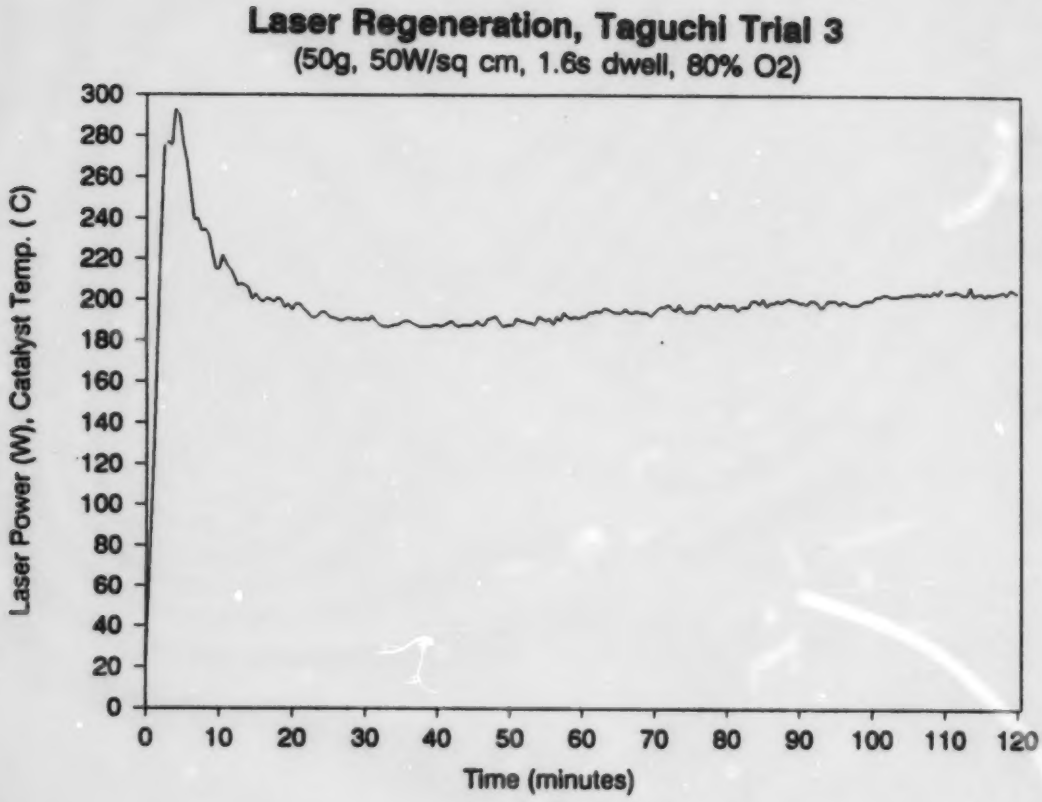


Figure 3.4: Catalyst bed temperature record during the laser regeneration of spent Shell 424 NiMo hydrotreating catalyst, matrix trial 3.

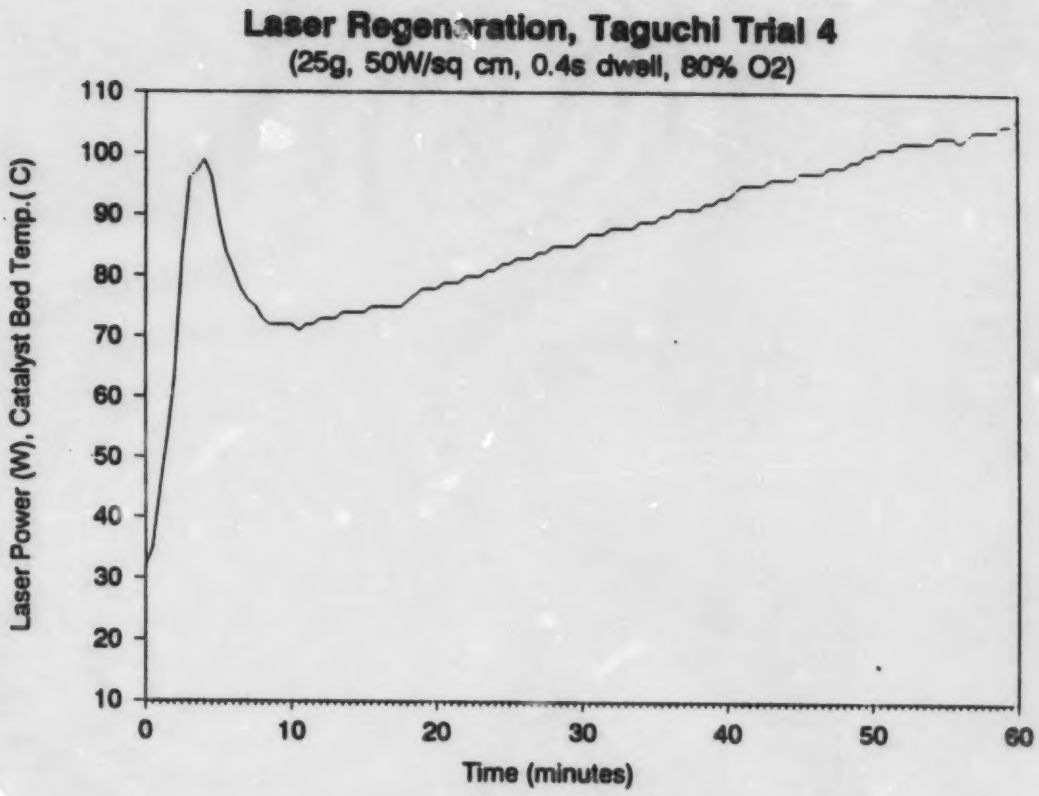


Figure 3.5: Catalyst bed temperature record during the laser regeneration of spent Shell 424 NiMo hydrotreating catalyst, matrix trial 4.

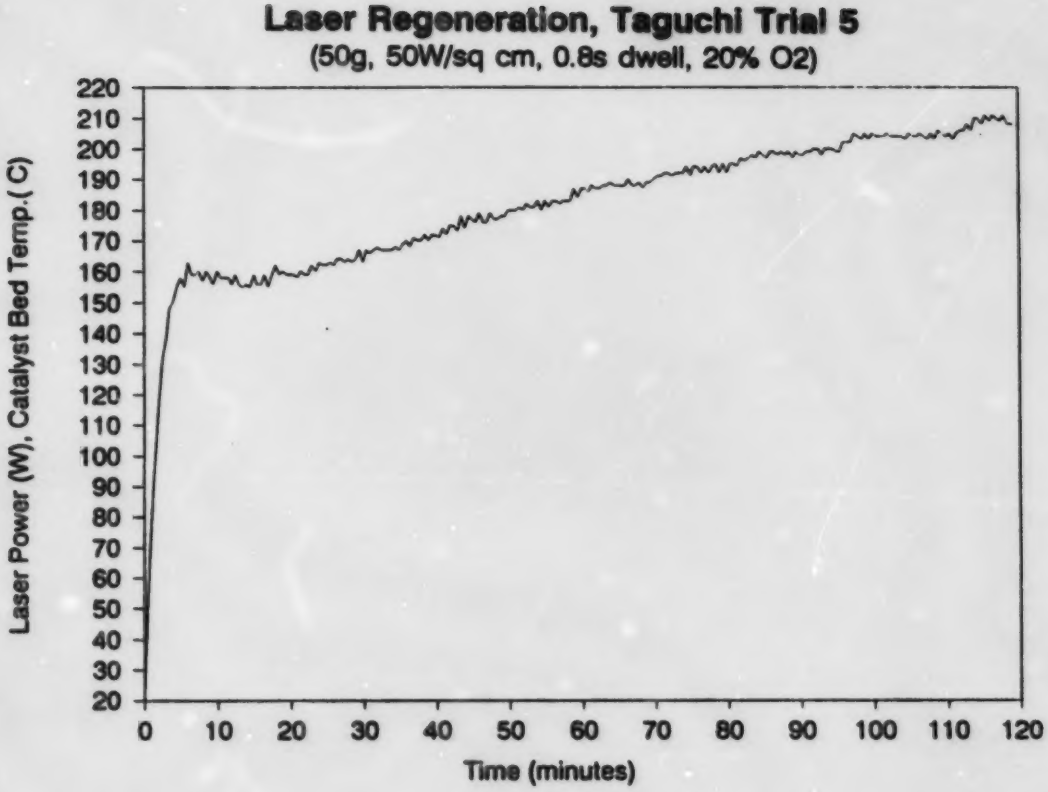


Figure 3.6: Catalyst bed temperature record during the laser regeneration of spent Shell 424 NiMo hydrotreating catalyst, matrix trial 5.

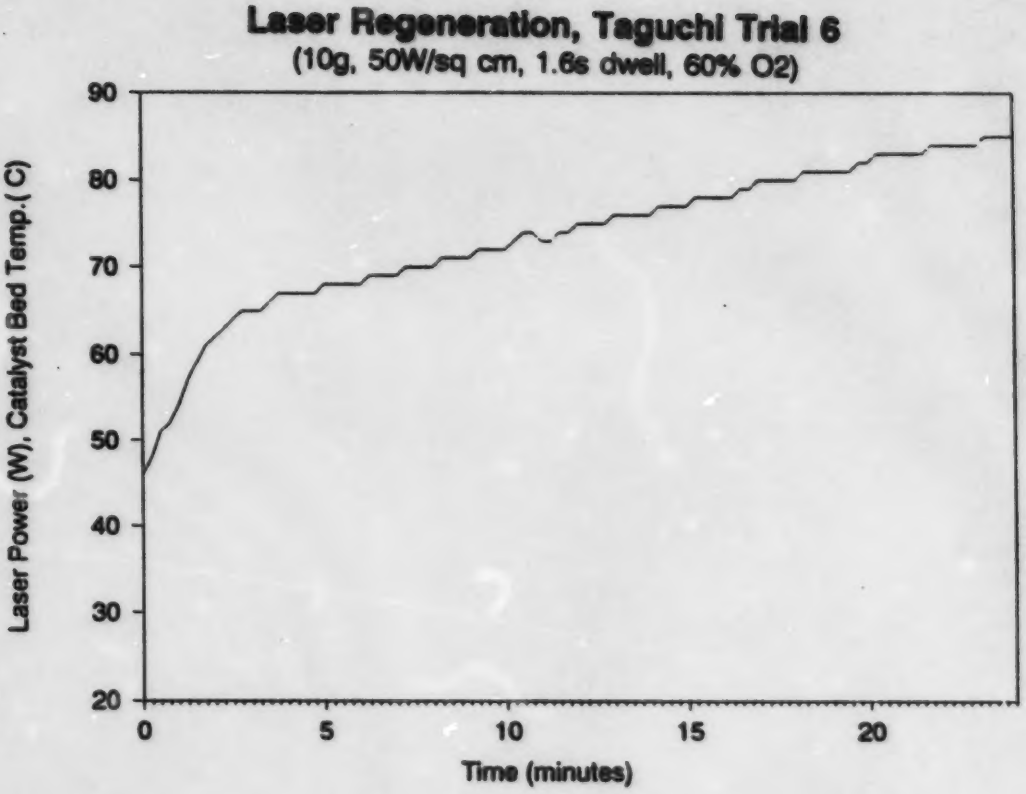


Figure 3.7: Catalyst bed temperature record during the laser regeneration of spent Shell 424 NiMo hydrotreating catalyst, matrix trial 6.

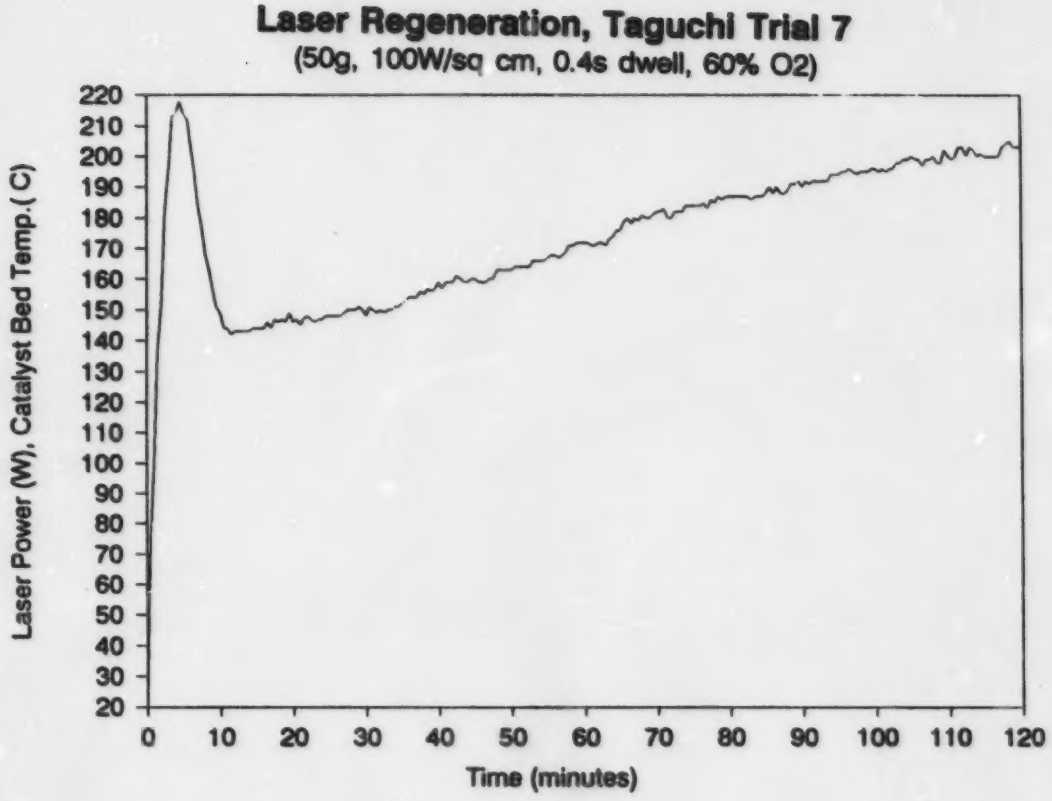


Figure 3.8: Catalyst bed temperature record during the laser regeneration of spent Shell 424 NiMo hydrotreating catalyst, matrix trial 7.

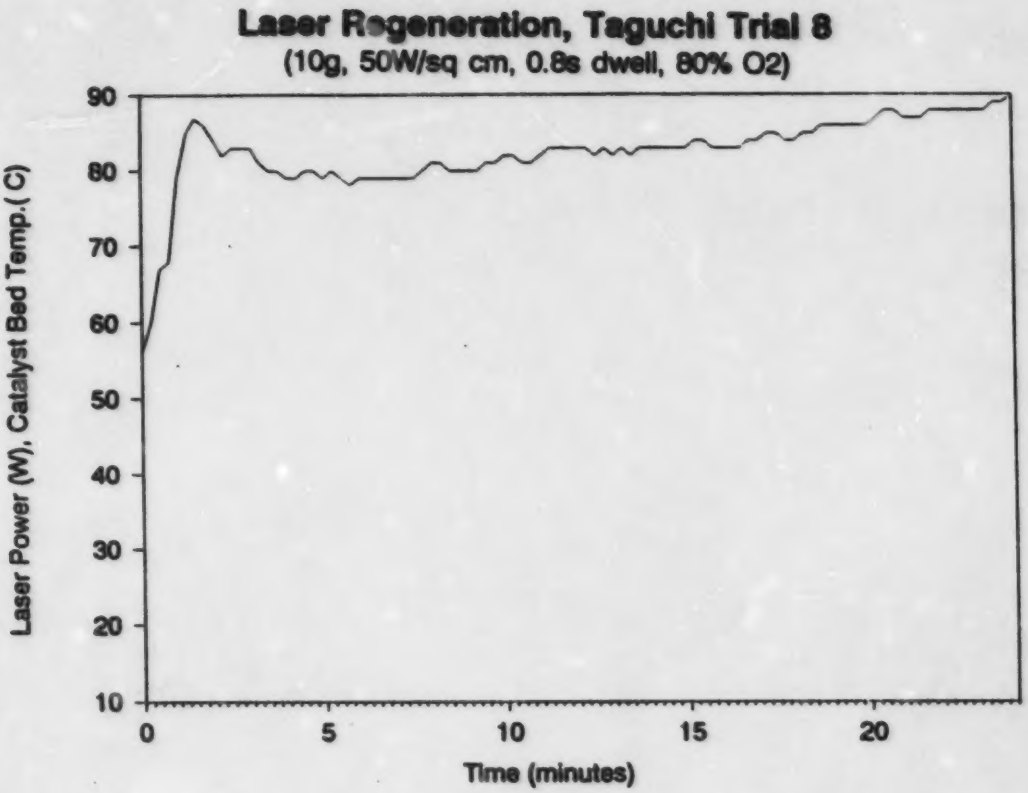


Figure 3.9: Catalyst bed temperature record during the laser regeneration of spent Shell 424 NiMo hydrotreating catalyst, matrix trial 8.

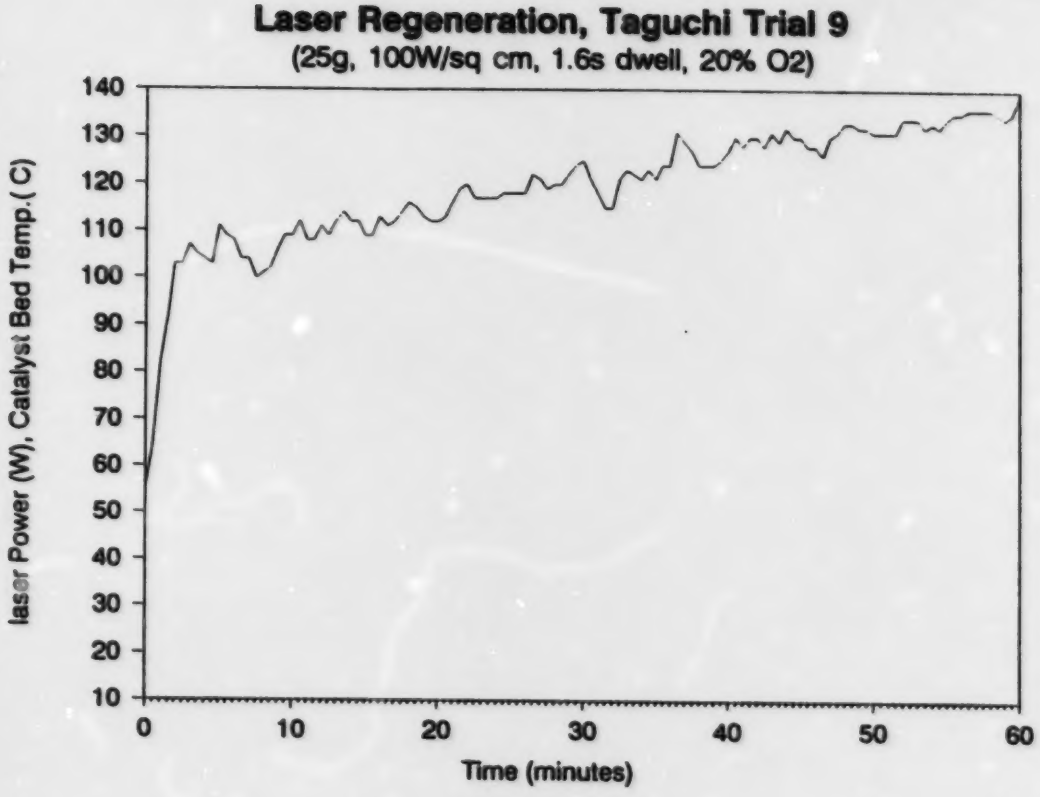


Figure 3.10: Catalyst bed temperature record during the laser regeneration of spent Shell 424 NiMo hydrotreating catalyst, matrix trial 9.

ature (figures 3.4, 3.5 and 3.9). Trial 7 (figure 3.8) which also had this peak did not lead to significant regeneration. The trials which led to measurable regeneration all have in common a moderate to long dwell time coupled with an enriched oxygen atmosphere. Trial 7 had both a low oxygen concentration (20%) and a short dwell (0.4 s), and this may explain the low level of regeneration in this case. This points out the fact that the sharp initial temperature rise is not indicative of the burn-off of a large portion of the fouling deposit. This initial temperature rise may be due to removal of lightly held, very reactive coke molecules and some sulphides.

3.1.1 Analysis of Regenerated Materials

The samples studied were characterized by observing their colour and physical appearance, microstructure (SEM), fractional regeneration and by measuring their crush strength, elemental composition, and infrared spectra. The physical characterization of laser regenerated catalyst materials from the matrix study is presented in table 3.1.

The colour variation in the regenerated materials is quite interesting. Most regenerated particles have a yellow-orange colouration. In many cases the colour is associated with a red-brown powder deposited on the surface of the particles. This orange-red colouration in many of the samples may be due to the presence of iron oxide. Iron is a common contaminant in hydrocarbon feedstocks along with nickel and vanadium. These materials are deposited in the catalyst particles as soluble metal-organic molecules that diffuse into catalyst pores and are decomposed. Due to the low diffusion rates of these molecules, iron content in used hydrotreating catalysts is generally concentrated in the outer one third of the particle radius. In spent catalyst material the iron is found in a sulphided state. Iron is also found to be present in high concentrations in attrited material (Bogdanor and Rase 1986). Incidentally, the presence of this iron is thought to lead to catalysis of both coke deposition and coke oxidation (Tomoyuki *et al.* 1982). In figure 3.11 a low magnification electron micrograph shows this reddish powder deposited in the grooves of a regenerated trilobed extrudate.

Trial No.	Regeneration Conditions				Physical Character ization	
	Mass (g)	I W/cm^2	Dwell (s)	$[O_2]$ %	Colour	Crush Strength (N)
1	10	35	0.4	20	black	98
2	25	35	0.8	60	brown	78
3	50	35	1.6	80	grey-orange	57
4	25	50	0.4	80	dark brown	98
5	50	50	0.8	20	brown	>127
6	10	50	1.6	60	grey-brown	110
7	50	100	0.4	60	grey-red	108
8	10	100	0.8	80	grey-yellow	78
9	25	100	1.6	20	grey-blue	>127

Table 3.1: Physical characterization of samples regenerated in the matrix study of laser regeneration.

Figure 3.11: Laser regenerated Ni/Mo trilobe extrudate showing iron-rich material deposited in grooves.

Indeed, PIXE elemental analysis confirms the presence of significant concentrations of iron in both coked and regenerated samples. The iron concentration was 0.58±.04% in the coked material, and was reduced to about 0.4% after conventional regeneration and to 0.25% after laser regeneration (average values, see table 3.2). Differences in the amount of iron removed during regeneration by the two methods may be due to the different methods of agitation. In the laser reactor the high flow of gas used for stirring entrains small particles produced by attrition. Since iron tends to concentrate in the outer region of the particles and is found in abundance in attrited material, this may be a source of loss for iron. In the conventional reactor the gas flow is much less turbulent, and iron present in small particles is more likely to be found adhering to the catalyst extrudates.

In laser regenerated materials which were exposed to higher intensities and longer dwell times, there is less evidence of surface deposits of iron rich material. This is not likely due to the absence of the deposits, but to the masking of that material by blue-green powder produced by the breakdown of the catalyst particles themselves. After these runs the interior of the laser reactor core was coated with a grey-green powder, which was presumably attrited catalyst material. This attrition was not seen when processing with laser intensities of the order of 50 W/cm^2.

The appearance of partially regenerated materials differed greatly when comparing conventional and laser methods. Conventionally regenerated materials showed a darker core with a gradual shading towards the outside of the catalyst extrudate. Partially laser regenerated materials showed a distinct boundary layer between an outer fully regenerated region and an inner completely coked region. This shell-like regeneration is precisely what is predicted for regeneration under strongly mass-transfer limited conditions (see section 1.1). The action of heat-transfer effects probably also contributes to this result. Although conventional regeneration shows some preference for burn-off in the outer parts of extrudates, there is much more uniformity in cross-sectional appearance of partially regenerated particles.

PIXE elemental analysis was performed on both the laser regenerated pre-trial and conventionally regenerated (CR1–3) selected samples, the results are given

in table 3.2. In this table the percent regeneration is given as determined by two different methods:PIXE and visual analysis. PIXE elemental analysis is not sensitive to light elements such as C, N, O, H etc., so there is no way to use these data to estimate the fraction of carbonaceous material removed. An estimate of the amount of coke removed was made by optical microscopic examination of broken extrudates. This measurement was made easier by the mechanism of laser regeneration which leads to a shell-like regeneration profile (see figure 1.2).

Due to mass and heat-transfer effects, there is a sharp boundary between two regions, regeneration apparently taking place only at an interface. Materials partially regenerated using the laser method show an outer region of fully regenerated material and an inner core which appears fully coked. In addition to this visual determination of the progress of regeneration, the reduction of sulphur concentration is also presented. Although sulphur is not a foulant, its removal by oxidative processes will give an indication of the progress of regeneration.

The extent of sulphur removal is equal or greater than the optically estimated percent regeneration in all cases. This is understandable from the TGA studies of catalyst regeneration performed. The removal of metal sulphides takes place at temperatures 100 to 150°C less than coke oxidation (see section 3.1.3, also Wukasch and Rase 1982). It should be noted that some samples which visually were 70-80% unregenerated had lost more than 90% of their sulphur content.

3.1.2 FTIR Spectroscopic Examination

The infrared spectra of hydrotreating catalysts in their oxidic state have been studied to some extent (Topsøe 1980, Lipsch and Schuit 1969a,b). There are a number of features which are well characterized and may be used to evaluate the chemistry of the catalyst surface. Unfortunately, alumina has a broad intrinsic absorption feature in the same region of the IR spectrum as that of the vibrational bands of MoO_3. This complicates the interpretation of the spectra in some cases since there is often saturation in this region. Table 3.3 compares the infrared features observed in laser regenerated Ni-Mo hydrotreating catalysts to known features of the component compounds of the catalyst material.

Sample	Regeneration Conditions				% Regeneration		Elemental Composition				
	Mass	I	Dwell	$[O_2]$	(visual)	(by [S])	[P]	[S]	[Fe]	[Mo]	[Ni]
	(g)	(W/cm^2)	(s)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
CR1	Conv. Regen. T_{max} 500°C				100	96	2.40	1.16	0.41	10.73	2.59
CR2	Conv. Regen. T_{max} 500°C				100	83	3.12	2.06	0.66	12.19	3.18
CR3	Conv. Regen. T_{max} 500°C				100	100	2.65	0.90	0.18	11.07	2.66
PT5	50	50	0.8	80	50	100	2.68	0.76	0.17	11.18	2.73
PT6	50	50	1.5	80	100	100	3.16	0.68	0.36	12.13	3.31
PT7	50	35	2.4	80	20-80	99	2.82	0.97	0.25	10.74	2.62
PT1	10	100	0.4	60	30	100	0.18	0.91	0.18	10.48	2.64
PT3	50	100	1.0	60	100	100	3.21	0.56	0.15	11.03	3.28

Table 3.2: PIXE elemental analysis of laser and conventional regeneration samples.

Table 3.3: Infrared spectral peak assignments for laser regenerated spent γ-Al_2O_3 supported Ni–Mo hydrotreating catalyst.

Catalyst Feature		Known Feature			
Maximum (cm^{-1})	FWHM (cm^{-1})	Maximum (cm^{-1})	FWHM (cm^{-1})	Compound	Vibration
Persistent features					
640-670	50-75	700;635;570	350;155;75	Al_2O_3;NH_4– MoO_3;Fe_xO_y	
960-1015	75-125	850,1000;700	130,20;350	MoO_3;Al_2O_3	
1210-1240	150-175	—	—	—	—
1600-1650	125-150	1590-1670	30-100	H_2O	deformation
2600→3700	~1100	3000-3700	varies	OH, H-bonded	stretch
Recurring features					
760-785	60	720-725	15-25	Fe_xO_y	—
850-860	30-50	850	130	MoO_3; also SH	—
1830-1850	60	1800-1850	—	alkenes?	
1940-1970	60	—	—	—	—
2215-2220	60	2400-2570		SH	—

The predominant state of Mo in Ni/Mo and Co/Mo catalysts is Mo^{6+} in the form of poly-molybdates and MoO_3 (Gajardo, Grange and Delmon 1980, Steel and Duley 1989). Spectra of these catalysts typically have peaks near 600, 820, 875 and 995 cm^{-1}. The spectrum is similar to that of bulk MoO_3, given in figure 3.12, with the exception of some peak broadening and a lack of feature definition. This is indicative of MoO_3 in an amorphous, microcrystalline or imperfectly crystalline state (Lipsch and Schuit 1969a). This observation coupled with large Mo peak intensities in the spectra of these catalysts serve to indicate that the molybdenum is present as a monolayer on the alumina surface. In addition to the features discussed above, there is also weak structure near 1100 cm^{-1} which is due to molybdenum in a tetrahedrally coordinated molybdate-like species.

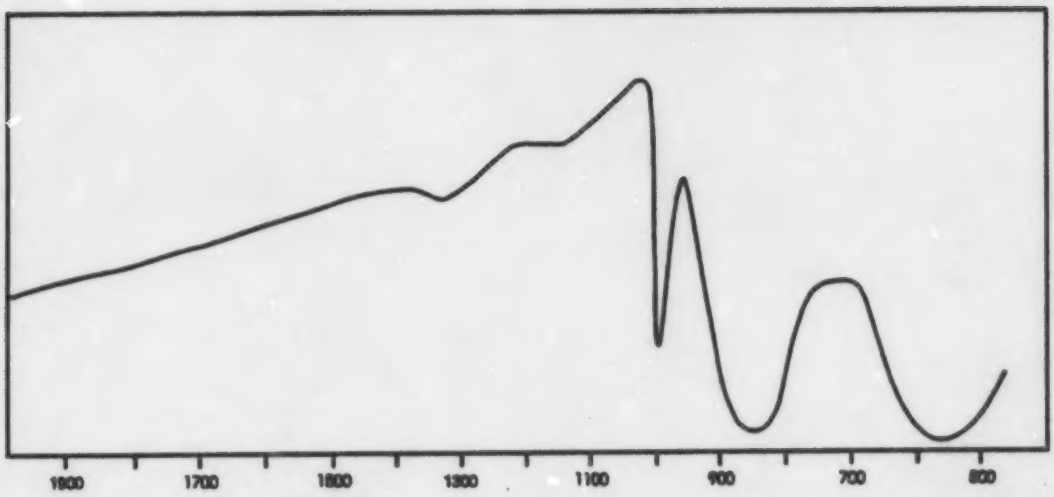


Figure 3.12: Infrared spectrum of MoO_3, from Nyquist and Kagel, 1971.

There do not appear to be any compounds formed with the promoters and molybdenum in hydrotreating catalysts. The infrared and UV-visible reflectance spectra of Co/Mo on γ-Al_2O_3 are lacking the resonances due to $CoMoO_4$ (Lipsch and Schuit 1969b). The spectra of Mo-oxide on promoted and un-promoted Mo catalysts are essentially identical. The presence of the promoter does not appear to affect the chemical or physical state of the molybdenum phase. It has been deduced that in these catalysts, Mo and the promoter ions are present in different compounds (Topsøe 1980, Lipsch and Schuit 1969b).

There are several different compounds of the promoters which may be present on the oxidic catalyst surface. In Co/Mo catalysts the Co may be present in an octahedral (Co^{2+}_{oct}) or a tetrahedral (Co^{2+}_{tet}) environment. Co^{2+}_{tet} has been shown to correspond to cobalt ions within the alumina support (Topsøe *et al.* 1986). These ions are mostly un-sulphided during catalyst use and do not participate in the catalytic activity. Co^{2+}_{tet} ions are produced in greater numbers at higher calcining temperatures.

The amount of octahedrally coordinated Co was shown to be directly proportional to the amount of catalytically active Co in the sulphided catalyst (Topsøe *et al. 1986*). Although not chemically bound, there does seem to be a correlation of the Co^{2+}_{oct} ions with Mo monolayer islands on the alumina surface (Topsøe and Topsøe 1982, Gajardo *et al.* 1980). Ultimately laser regenerated materials must be studied in the sulphided state to determine whether the Mo and promoter oxides are in the correct chemical and physical relationship to lead to production of the active Co-Mo-S (or Ni-Mo- S) phase structures.

It has been noted previously (Steel and Duley 1989) that an intense blue colouration of laser heated Co/Mo catalysts may be related to the presence of Co ions in tetrahedral sites as $CoAl_2O_4$ or in octahedral holes of γ-Al_2O_3. This need not indicate a major problem with laser regeneration since concentrations of Co at the ppm level could provide this intense colouration. In addition by changing the sulphidation conditions it is possible to retrieve these ions. Delmon (1986) notes that high temperature sulphiding leads to a dramatic reduction in the intensity of the Co^{2+}_{tet} absorption bands at 550, 590 and 625 nm.

Unfortunately, the mass concentration of the promoters is so small that very

low signal strength is obtained for the IR bands of these materials. This is compounded by the incorporation of some of the promoter materials in the bulk of the support. The correlation of Co (Ni) ions with the MoO_3 monolayer is thought to be due to the preferential location of promoter ions below molybdenum oxide islands (Delmon, 1986). This arrangement of the promoter oxides would also mask them from analysis.

The infrared spectrum of a sample of spent Shell 424 Ni/Mo hydrotreating catalyst is given in figure 3.13

There is strong absorption over a broad spectral range. Reflectance is below 2% from 400 to 4000 wavenumbers. Graphitic materials have small band gaps and are broad-band absorbers (Robertson and O'Reilly 1987). This very broad absorption is thus associated with material in the coke layer. There are a number of features which show through this broad absorption band. For example, the bending vibration of physically adsorbed water absorbs at 1600 cm^{-1}, there are metal-oxygen vibrational transitions at 800-1200 cm^{-1}, and there are a number of surface hydroxyl peaks at 3000 to 3600 cm^{-1}. The peaks at 2940 and 1450 cm^{-1} correspond to C–H vibrations of coke molecules and residual hydrocarbons.

The spectrum of an unused sample of Ni/Mo hydrotreating catalyst is given in figure 3.14.

Reflectance from this sample is in general much higher than from the spent catalyst. In the long wavelength extreme of the figure, where coke was strongly absorbing, the reflectance of unused catalyst is about 20%. The spectrum shows a strong, broad feature maximizing at 3450 cm^{-1}, this is due to hydroxyl groups on the hydrated oxide surface. The peak at 1630 is due to the bending vibration of loosely held water molecules. While the peak at 1420 cm^{-1} is due to the presence of some residual precursor material. The features near 1000 and 1150 cm^{-1} arise from metal-oxygen or metal-hydroxide vibrations in the support and active metal oxide materials.

The feature at 995 cm^{-1} may unambiguously be associated with MoO_3 vibrations (Nyquist and Kagel 1971, Lipsch and Schuit 1969a,b). The feature at 1100-1200 cm^{-1} is more difficult to as[illegible]The edge of the Al_2O_3 absorption, which extends to 500 cm^{-1}, is between 1000 and 1100 cm^{-1}, this broad band may

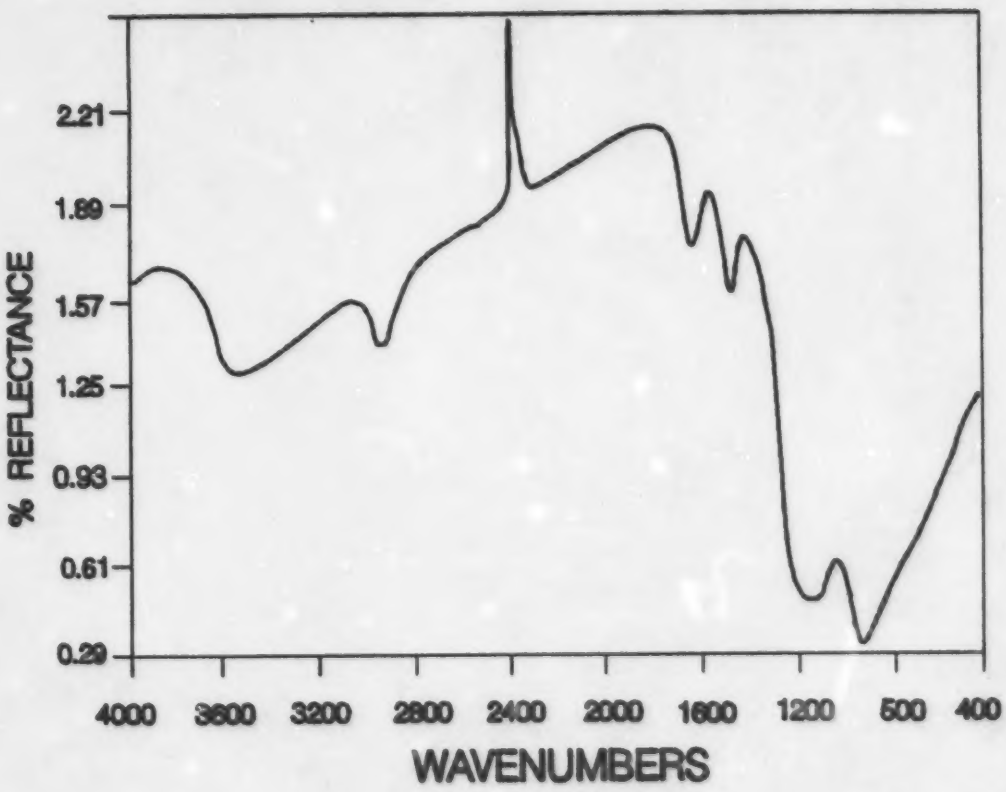


Figure 3.13: Infrared spectrum of coked-spent Shell 424 Ni/Mo hydrotreating catalyst.

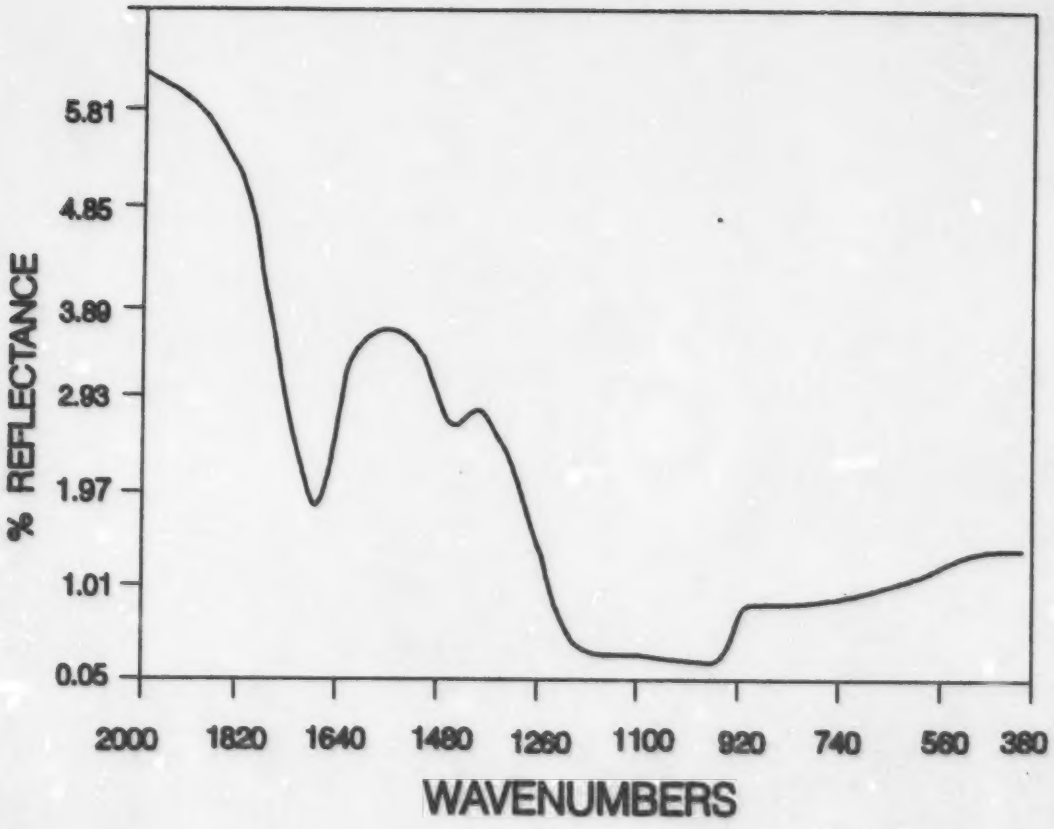


Figure 3.14: Infrared spectrum of unused Ketjenfine Ni/Mo hydrotreating catalyst.

contribute to the 1150 cm^{-1} feature. The presence of the band near 1100 cm^{-1} in unused catalyst removes fears that this band indicates aluminum sulphate formation. This compound once formed is a permanent contaminant of hydrotreating catalysts.

The structure below 800 cm^{-1} is due primarily to MoO_3, the lack of structure in this region for many of the samples studied is due to the micro-crystalline or amorphous nature of MoO_3 in these catalysts.

Spectra of laser regenerated materials are very similar to that of unused materials. The reflectance is generally restored to 15-20% in regions without strong absorption features. This is due to the near complete removal of the broad-band absorption of the coke deposits. Features due to the C–H vibration in coke molecules (2950 and 1450 cm^{-1}) are completely removed in all samples which were judged 100% regenerated by optical estimation. A sample spectrum of laser regenerated material is given in figure 3.15.

By visual appearance this sample was incompletely regenerated, but 99% of the sulphur had been removed (see RF3 in table 3.2). Since there is very little evidence of coke absorption in the IR spectrum, very small amounts of carbonaceous deposit must lead to substantial discolouration in partially regenerated extrudates.

3.1.3 Conventional Regeneration

A thermogravimetric analysis was performed on the coked catalyst to determine at which temperatures the bulk of the fouling materials would be oxidized. A plot of total weight loss versus reactor temperature is presented in figure 3.16.

The fouling layer on the catalyst, including sulphur in the metal sulphides, corresponds to about 22% by mass of the spent material. By far the largest component was sulphur which accounted for about 2/3 by mass of the material removed. The carbonaceous deposit corresponded to about 9% by mass of the catalyst in oxide form.

There are three major mass loss features in the TGA plot. Analysis of the evolving gases shows that the first peak at 125°C is due to the removal of phys-

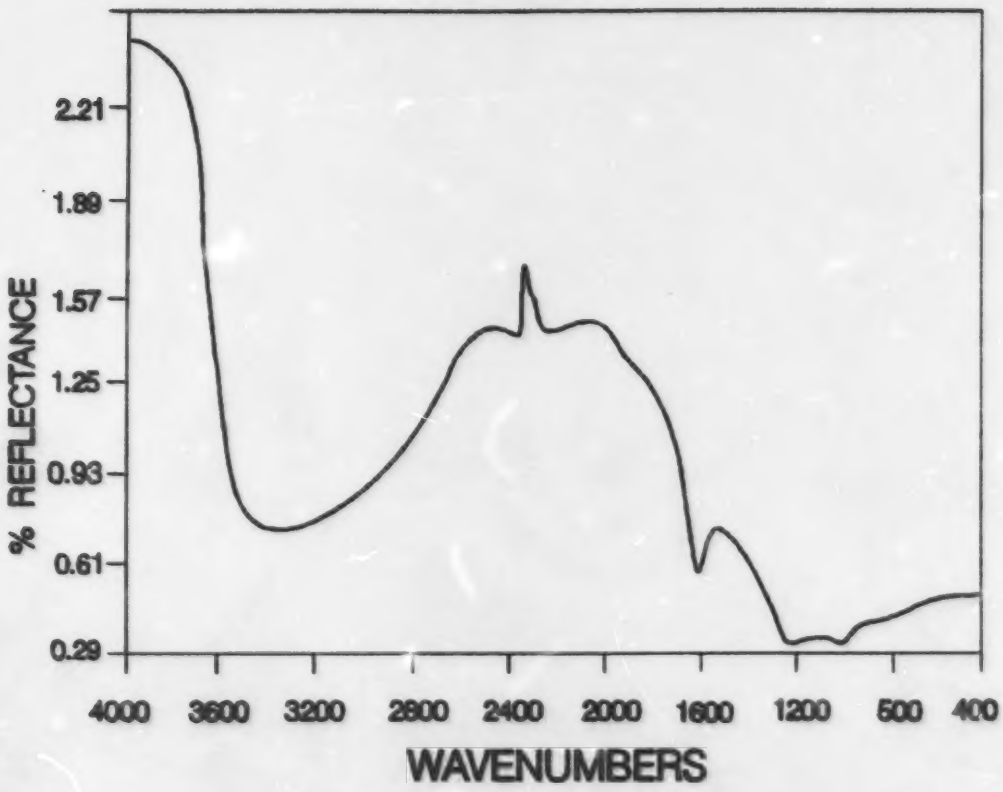


Figure 3.15: Infrared spectrum of laser regenerated Ni/Mo hydrotreating catalyst; I=35 W/cm^2, 80% O_2, τ=2.4s.

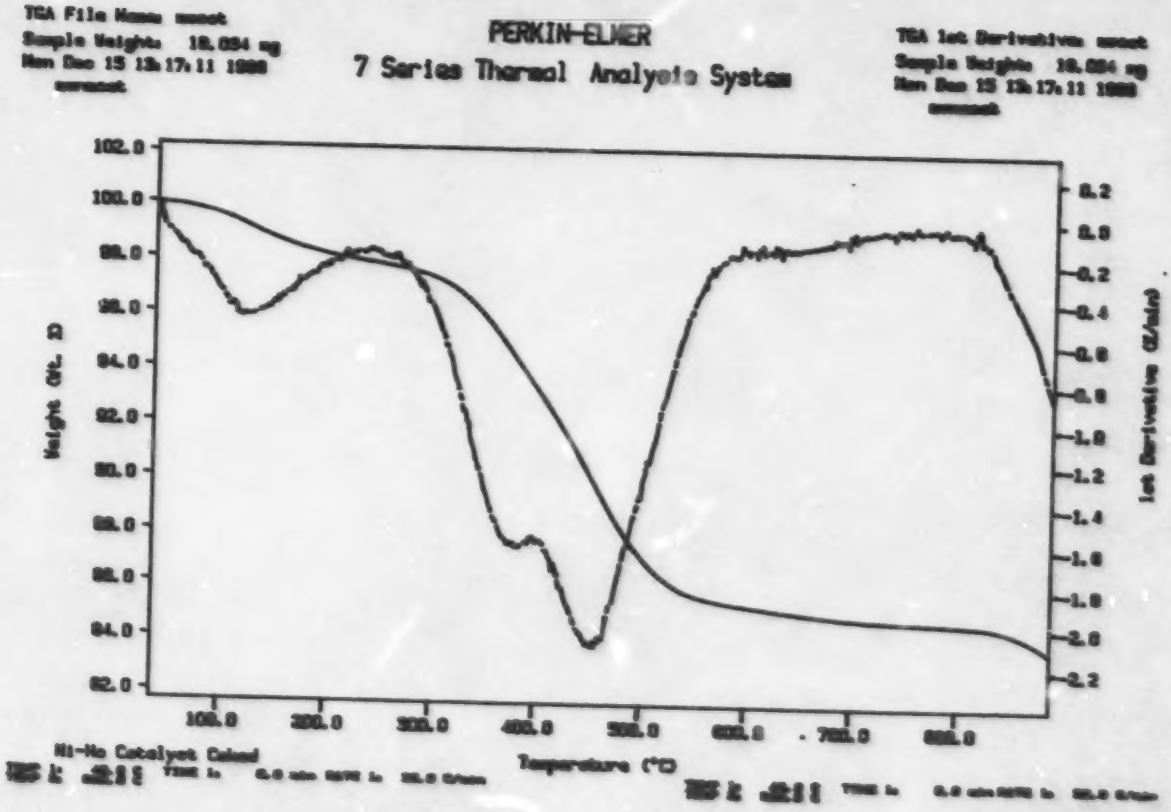


Figure 3.16: Total mass loss of spent Ni/Mo catalyst as a function of temperature, TGA analysis.

ically adsorbed water. The second at 375°C is due to sulphide loss as indicated by SO_2 evolution which peaks at 310°C. The removal of easily oxidized coke molecules also contributes to this mass loss feature as indicated by an H_2O evolution peak, and low temperature shoulders in CO_2, CO and COS evolution, which peak at higher temperatures. The third mass loss peak at 460°C corresponds to the removal of more strongly held coke molecules and residual sulphur compounds. The catalyst has been cleaned of about 93% by mass of all fouling materials by heating to 550°C. This is the maximum regeneration temperature which is generally used conventionally.

Conventional regeneration was performed in the furnace described in section 2.1.3. The maximum temperature used was 550°C, and the temperature ramping was between 2 and 10°C/min. Physical characterization of a few of the runs performed are given in figure 3.1, and elemental analysis of these samples was given in figure 3.2. In the table below the elemental concentrations averaged over the laser and conventionally regenerated samples are given.

Method	% Regen by[S] (%)	$[P]_{avg}$ (%)	$[Fe]_{avg}$ (%)	$[Mo]_{avg}$ (%)	$[Ni]_{avg}$ (%)
Furnace	93	2.72	0.42	11.3	2.81
Laser	92	2.80	0.25	11.0	2.83

Elemental analysis of conventionally regenerated material shows similar active metal concentrations to laser regenerated material. The average extent of regeneration as measured by sulphur loss, is equivalent for both methods, even though only those samples processed under the most harsh conditions led to complete removal of carbonaceous deposits in the laser reactor.

The extent of visual regeneration of these materials was usually 100% for completed runs with more than 1 hour exposure to 500°C. The interior of conventionally regenerated Ni/Mo extrudates was a uniform yellow colour with reddish discolouration near the outer edge. As discussed previously this discolouration is due to oxides of iron, a common contaminant in the feeds used in hydrotreating.

Table 3.4: Characterization of conventionally regenerated (CR) Ni/Mo catalyst.

Sample	Regeneration Conditions	Physical Characterization		
		Colour	% Regen.	Crush Strength (N)
CR1	furnace T_{max} =500°C	yellow-brown	100	>127
CR2	furnace T_{max} =500°C	yellow-brown	100	103
CR1	furnace T_{max} =500°C	beige	100	103
KJF	unused NiMo	green-yellow	—	40

An FTIR spectrum of a conventionally regenerated Ni/Mo hydrotreating catalyst is given in figure 3.17.

In this spectrum, all of the features of unused catalyst are reproduced. There is high reflectance at short wavelengths, no evidence of $-CH_3$ or $-CH_2-$ vibrational bands, and the expected structure in the metal-oxygen vibrational region is present. In table 3.5 the assignments of the various peaks in the infrared spectra of conventionally calcined Ni/Mo hydrotreating catalyst are given.

Table 3.5: Infrared spectral peak assignments for conventionally regenerated spent γ-Al_2O_3 supported Ni–Mo hydrotreating catalyst.

Catalyst Feature		Known Feature			
Maximum (cm^{-1})	FWHM (cm^{-1})	Maximum (cm^{-1})	FWHM (cm^{-1})	Compound	Vibration
Persistent features					
970-995	80	950-995	80	MoO_3	—
1220-1270	150-200	—	—	—	—
1615-1650	80-100	1590-1670	30-100	H_2O	deformation
2600→3800	~1200	3000-3700	varies	OH,H-bonded	stretch
Recurring features					
710-775	~150	720-725	15-25	Fe_xO_y	

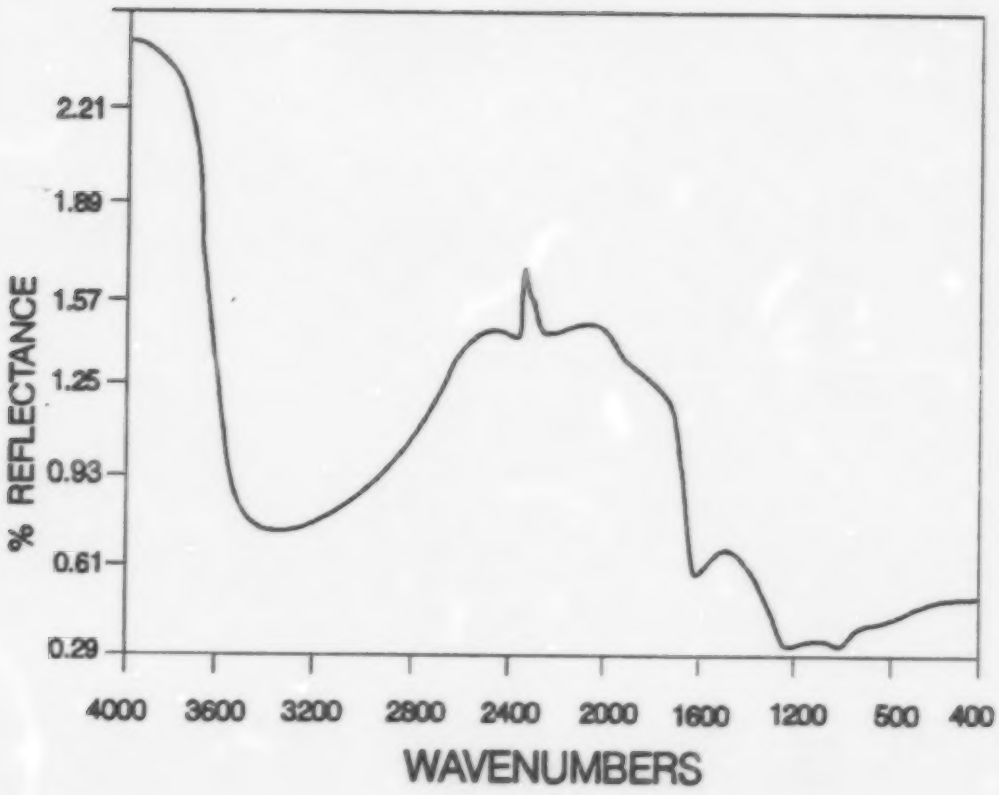


Figure 3.17: Infrared spectrum of conventionally regenerated Ni/Mo hydrotreating catalyst; 300°C for 3 hours and 500°C for 1.5 hours, air flow 10 l/min.

3.2 Analysis of Results

3.2.1 Background on Taguchi Method

The purpose of this section is to familiarize the reader with terminology and analysis methods of the Taguchi experimental design technique.

In laying out a test and development strategy, simple logic will usually be sufficient to establish all possible combinations of factors along with allowable ranges of each of the factors involved. but for larger projects involving many factors, the number of possible combinations is prohibitively large. In addition, higher order interactions among the influencing factors may be influential for specific projects. A customary method of reducing the number of test combinations is to use what are known as partial factorial experiments. Taguchi constructed a special set of general designs for factorial experiments that cover many applications. The special set of designs consist of orthogonal arrays. The use of these arrays helps determine the least number of experiments needed for a given set of factors.

For this project an L_9 Taguchi array was used. This orthogonal array has 9 trials 4 factors and 3 levels (see section 2.3). The objective of the analysis of the Taguchi experimental results is primarily to seek answers to the following three questions.

1. What is the optimum condition?
2. Which factors contribute to the results and by how much?
3. What will be the expected result at the optimum condition?

Table 3.6 lists the factors, levels and associated responses for % regeneration, pore volume and pore area of the laser regenerated catalysts. A Taguchi analysis for each response is outlined below.

3.2.2 Laser Regeneration Response

Level Totals and Their Averages for % regeneration

	FACTORS				RESULTS		
TRIAL	A	B	C	D	%R	P.V.	P.A.
2	1	2	2	2	7	0.258	135.2
3	1	3	3	3	100	0.354	119.4
4	2	1	2	3	59	0.239	129.3
5	2	2	3	1	5	0.292	146.8
6	2	3	1	2	78	0.256	126.6
7	3	1	3	2	97	0.312	138.9
8	3	2	1	3	100	0.294	113.6
9	3	3	2	1	89	0.295	109.0

Table 3.6: Results of the Taguchi trials, %R, P.V. and P.A. stand for % regeneration, pore volume and pore area respectively. Factors A,B,C and D represent radiation intensity, dwell time, packing density and oxygen concentration respectively.

The factor averages at each factor level are obtained by adding the results of all trial conditions at the level considered, and then dividing by the numbers of data points added.

$\overline{A}_1 = (y_1 + y_2 + y_3)/4 = (2 + 7 + 100)/4 = 36.33$

$$\overline{A}_1 = 36.33 \quad , \quad \overline{A}_2 = 47.33 \quad , \quad \overline{A}_3 = 95.33$$
$$\overline{B}_1 = 52.67 \quad , \quad \overline{B}_2 = 37.33 \quad , \quad \overline{B}_3 = 89.00$$
$$\overline{C}_1 = 60.00 \quad , \quad \overline{C}_2 = 51.67 \quad , \quad \overline{C}_3 = 67.33$$
$$\overline{D}_1 = 32.00 \quad , \quad \overline{D}_2 = 60.67 \quad , \quad \overline{D}_3 = 86.33$$

The figure 3.18 below shows the "main effects" or average performance of factors involved. The difference between the average value of each factor at different levels indicates the relative influence of the effect. The larger the difference, the stronger the influence. The sign of the difference, obviously indicates whether the change from one level to the other increases or decreases the result.

Total of all results: T=537

Correction Factor (CF)

CF=$T^2/n = 32,041$, where n is equal to the number of trials.

Total sum of squares

Total sum of squares gives an estimate of the sum of the variations of the individual observations about the mean of the experimental data and the variation of the mean about the target value.

$$S_T = \left(\sum_{i=1}^{9} y_i^2\right) - CF = 14,932$$

Factor sum of squares

$$S_A = A_1^2/N_{A1} + A_2^2/N_{A2} + A_3^2/N_{A3} - CF$$

Where A_1 is the total number of results where factor A is at level 1 and N_{A1} is the total number of experiments in which factor A_1 is present. The sum of squares is a measure of the deviation of the experimental data from the mean value of the data. Summing each squared deviation emphasizes the total deviation.

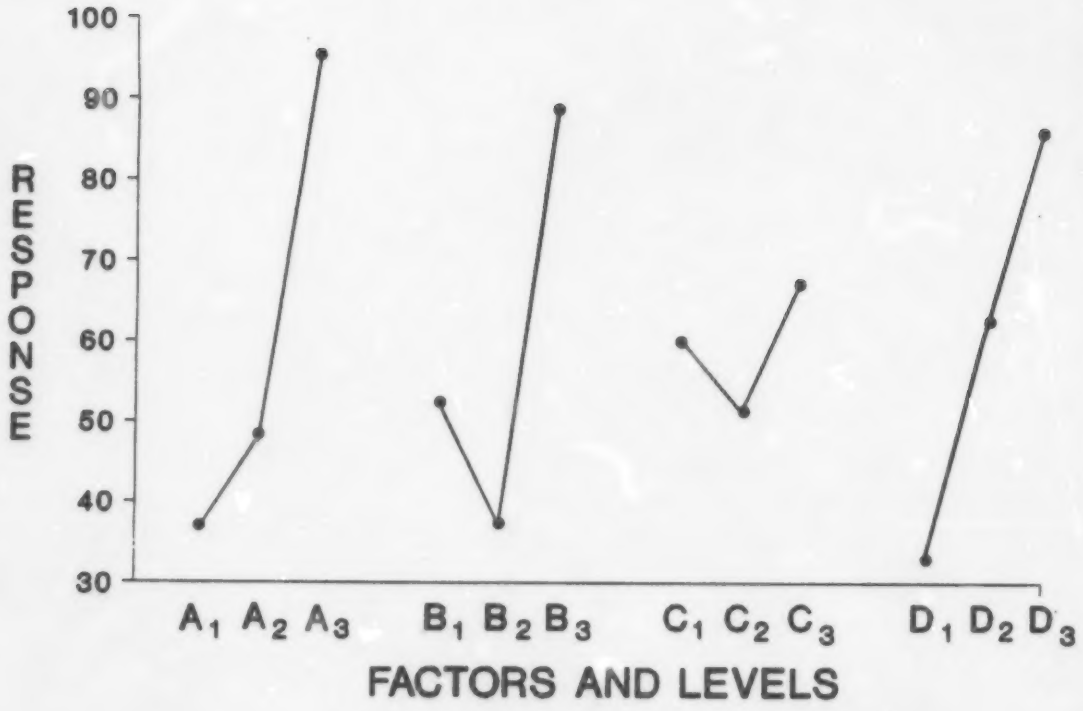


Figure 3.18: The main effects for the % regeneration response

$S_A = 5,906$
$S_B = 4,224$
$S_C = 368$
$S_D = 4,432$

Degrees of freedom factor

It is a measure of the amount of information that can be uniquely determined from a given set of data. Degrees of freedom for data concerning a factor equals one less than the number of levels. f_A = (Number of levels of factor A) − 1

$$f_A = f_B = f_C = f_D = 2$$

Variance

Variance measures the distribution of the data about the mean of the data. Since the data is representative of only a part of all possible data, Degrees of freedom rather than the number of observations is used in the calculation.

$V_A = S_A/f_A = 2,953$
$V_B = S_B/f_B = 2,112.34$
$V_C = S_C/f_C = 184.34$
$V_D = S_D/f_D = 2,216.33$

Percentage Contribution

$P_A = 100 \times S_A/S_T = 39.55$
$P_B = 100 \times S_B/S_T = 28.29$
$P_C = 100 \times S_C/S_T = 2.47$
$P_D = 100 \times S_D/S_T = 29.69$

3.2.3 Pore Volume Response

Level Totals and Their Averages for pore volume

$\overline{A}_1 = (y_1 + y_2 + y_3)/4 = 768/4 = 256.00$

$$\overline{A}_1 = 0.256 \quad , \quad \overline{A}_2 = 0.262 \quad , \quad \overline{A}_3 = 0.300$$
$$\overline{B}_1 = 0.235 \quad , \quad \overline{B}_2 = 0.281 \quad , \quad \overline{B}_3 = 0.301$$
$$\overline{C}_1 = 0.235 \quad , \quad \overline{C}_2 = 0.264 \quad , \quad \overline{C}_3 = 0.319$$
$$\overline{D}_1 = 0.247 \quad , \quad \overline{D}_2 = 0.275 \quad , \quad \overline{D}_3 = 0.295$$

The figure 3.19 shows the "main effects" or average performance of factors involved.

Total of all results: T=2.456

Correction Factor (CF)

CF= $T^2/n = 0.67022$ where n is equal to the number of trials

Total sum of squares

$$S_T = \left(\sum_{i=1}^{9} y_i^2\right) - CF = 0.02473$$

Factor sum of squares

$$S_A = A_1^2/N_{A1} + A_2^2/N_{A2} + A_3^2/N_{A3} - CF$$

Where A_1 is the total number of results where factor A is at level 1 and N_{A1} is the total number of experiments in which factor A_1 is present.

$S_A = 0.00344$

$S_B = 0.00685$

$S_C = 0.01093$

$S_D = 0.00348$

Degrees of freedom factor

f_A = (Number of levels of factor A) − 1

$$f_A = f_B = f_C = f_D = 2$$

Variance

$V_A = S_A/f_A = 1.720 \times 10^{-3}$

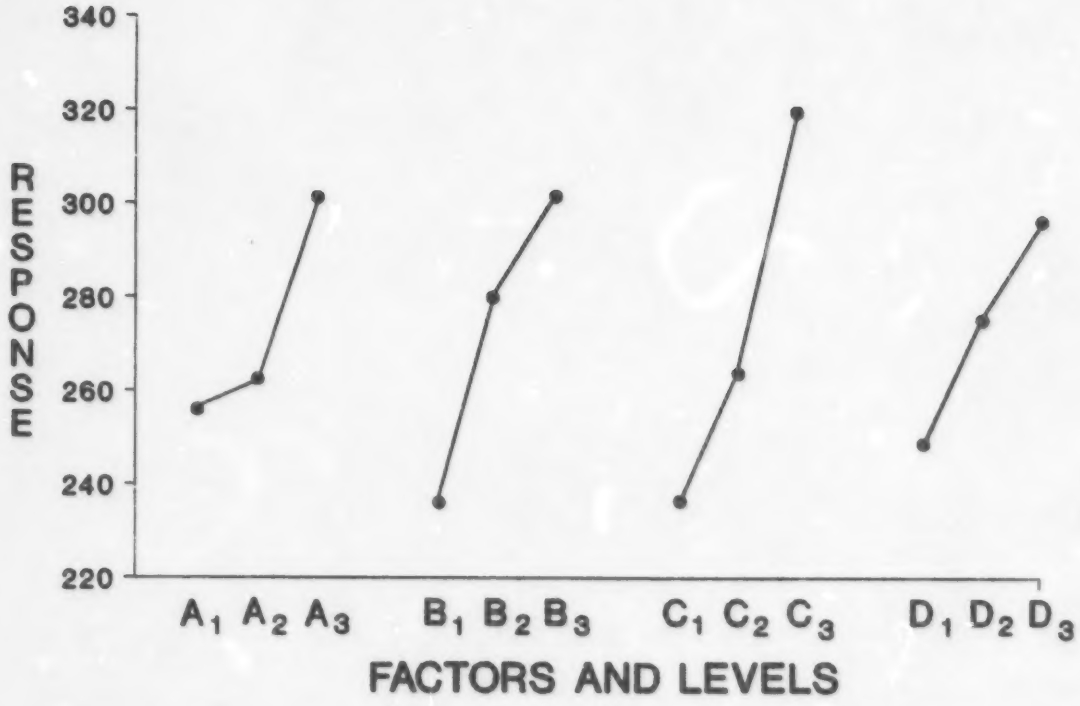


Figure 3.19: The main effects for the pore volume response

$V_B = S_B/f_B = 3.425 \times 10^{-3}$
$V_C = S_C/f_C = 5.465 \times 10^{-3}$
$V_D = S_D/f_D = 1.740 \times 10^{-3}$

Percentage Contribution
$P_A = S_A/S_T = 13.92$
$P_B = S_B/S_T = 27.70$
$P_C = S_C/S_T = 44.20$
$P_D = S_D/S_T = 14.08$

3.2.4 Pore Area Response

Level Totals and Their Averages for pore area
$\overline{A}_1 = (y_1 + y_2 + y_3)/4 = 344.30/4 = 114.77$

$$\overline{A}_1 = 114.77 \quad , \quad \overline{A}_2 = 134.23 \quad , \quad \overline{A}_3 = 120.50$$
$$\overline{B}_1 = 119.30 \quad , \quad \overline{B}_2 = 131.87 \quad , \quad \overline{B}_3 = 118.33$$
$$\overline{C}_1 = 109.97 \quad , \quad \overline{C}_2 = 124.50 \quad , \quad \overline{C}_3 = 135.03$$
$$\overline{D}_1 = 115.17 \quad , \quad \overline{D}_2 = 133.57 \quad , \quad \overline{D}_3 = 120.77$$

The figure 3.20 below shows the "main effects" or average performance of factors involved.

Total of all results: T=1108.50

Correction Factor (CF)

CF= $T^2/n = 136,530.25$ where n is equal to the number of trials

Total sum of squares

$$S_T = \left(\sum_{i=1}^{9} y_i^2\right) - CF = 2,426.70$$

Factor sum of squares

$S_A = 600.43$
$S_B = 342.01$

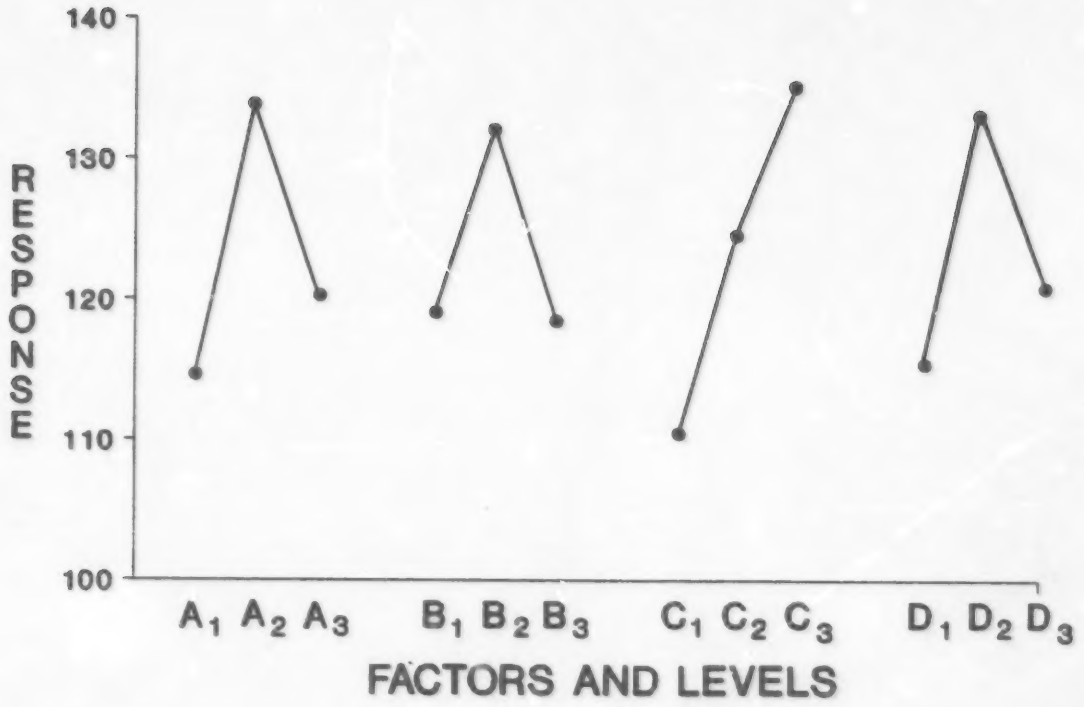


Figure 3.20: The main effects for the pore area response

$S_C = 950.51$
$S_D = 533.76$

Degrees of freedom factor

f_A = (Number of levels of factor A) − 1

$$f_A = f_B = f_C = f_D = 2$$

Percentage Contribution

$P_A = S_A/S_T = 25$
$P_B = S_B/S_T = 14$
$P_C = S_C/S_T = 39$
$P_D = S_D/S_T = 22$

This study attempts to predict the answers to the following questions; "how good are the regenerated catalysts" and "what are the optimum values for each factor involved". The most direct answer to these questions can be obtained by using the regenerated catalysts in an actual hydrocracking procedure and analyzing the results. Since this method of analysis is not available to us at the present time an alternate means of analysis was developed. To this end, three characteristics of the regenerated catalysts, namely % regeneration, pore volume and pore area were analyzed. Using the Taguchi method, optimum values for each response was predicted. The results of all three responses have to be optimized with respect to each other to obtain a meaningful conclusion.

The degree of regeneration of the laser processed catalyst was determined using PIXE analysis. The sulphur content of both the new and the regenerated catalyst samples are used as an indicator of regeneration level since during operation as a catalyst a large portion of the active metals and promoters are in a sulfided form (Furimsky 1988) The presence of sulphur in laser regenerated catalysts therefore provides an indicator of the potential catalytic activity of these materials. It is significant that sulfur is retained on a laser regenerated catalysts but is usually removed during conventional regeneration thus requiring an additional presulfiding treatment. This additional treatment is not required in laser

regeneration.

According to the % regeneration data the optimum laser regeneration is obtained during trials 3, 7, 8 and 9. The percent contributions of the factors involved indicate that the laser radiation intensity and the oxygen content of the reactor are the dominant factors for this response.

In figure 3.21 the total pore volume of the regenerated catalysts are plotted against the total pore area. The results show a linear correlation between these variables. Trials 3, 9 and 8 lie off the linear regression line of the remainder of the data. When the factor levels of these trials are correlated to the % regeneration it is clear that during these regenerations the conditions were very severe (high intensity, duration and oxygen content). Even though the regeneration percentages for these trials are seemingly very high the pore volume and pore area data suggest that during these runs pore area was lost through sintering and destruction of small pores. Further more the pore area and pore volume Taguchi study shows that the most significant factor for these responses is the packing density. When this is contrasted to the most significant contributions indicated by the Taguchi analysis of % regeneration, the indication of sintering becomes clearer since high packing densities prevent the catalysts from sintering.

Based on these observations the optimum regeneration condition seems to be a combination of high laser radiation intensity (100 W/cm^2), short dwell time (0.4 s), high packing density (50 g) and medium oxygen content (60%).

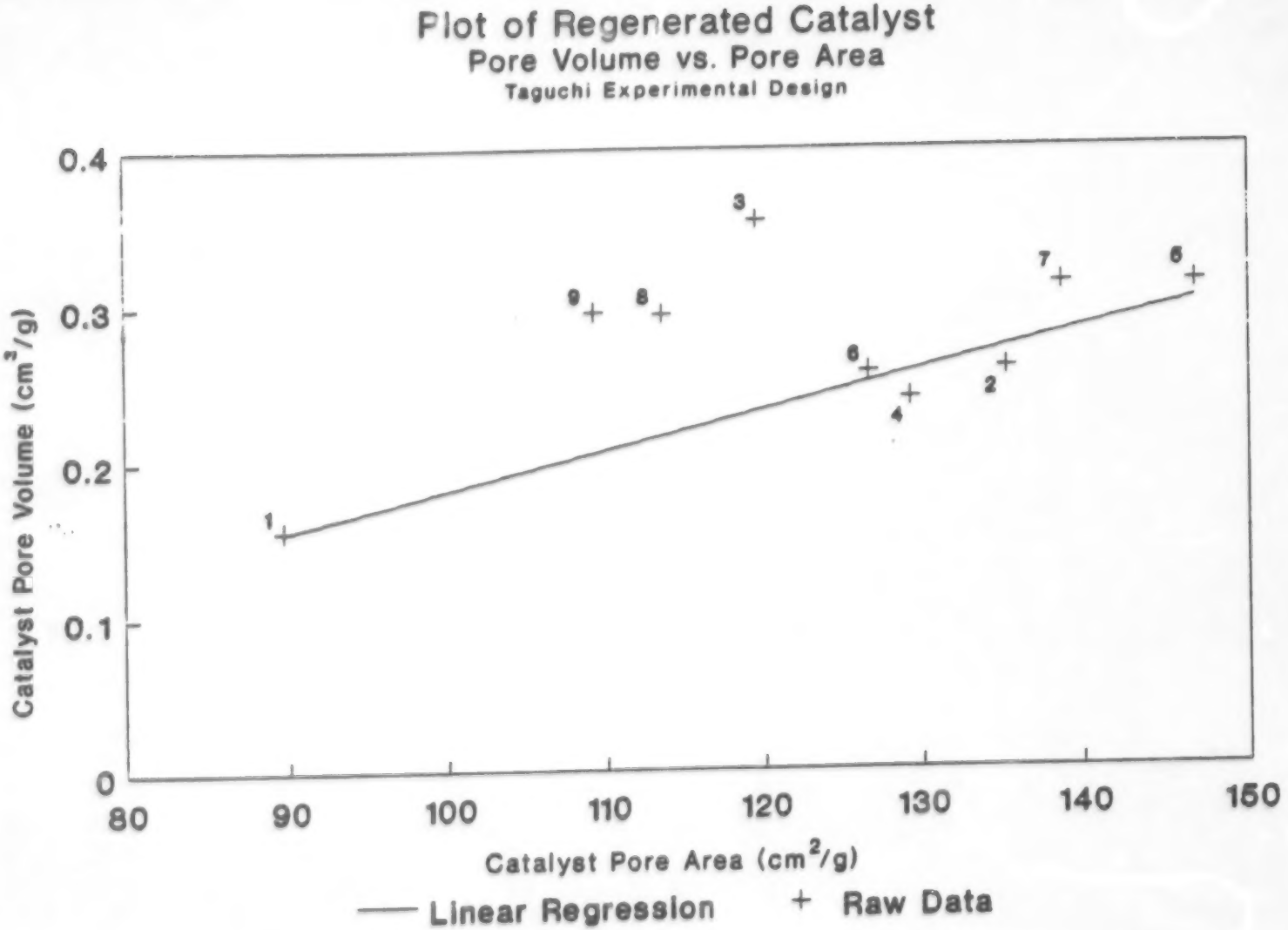


Figure 3.21: Total pore volume versus total pore area for various laser regeneration Taguchi trials. The numbers near the data points indicate the Taguchi trial number.

3.3 Economic Feasibility

Absolute comparison of the cost and benefits of the laser based regeneration method with the conventional technology must be between systems which are fully optimized, and capable of processing commercially significant amounts of material. This study must await further investigation including the engineering and development of a larger, pilot-plant sized laser regeneration system. After this work has been performed a true comparison of the capital costs may be achieved. The economics of running the bench-scale laser system are attractive and show that operating cost upon scale-up will likely be competitive with conventional burn-off.

In the bench scale regeneration units assembled for this project, gas consumption and materials handling costs are similar. The cost of the thermal energy used in the combustion of foulants is the primary source of comparison of the operating cost of the two regeneration methods.

Full regeneration of 50g batches is obtained with the laser regenerator with total output power of 110 W, and a run time of 1.5 to 2 hours. The efficiency of the laser tubes has been up to 15%, which gives a wall-plug energy consumption of 1.1-1.5 kWh, or 22-30 kWh/kg. This result is encouraging, and at current rates (~$0.05/kWh) leads to an energy cost of about $1.50/kg of regenerated catalyst. The efficiency of the laser process will increase as the operating parameters are further optimized by refinement of the laser based method.

Conventional regeneration using the bench-scale furnace reactor, involved gradually increasing the catalyst temperature from room temperature up to 500°C over a period of several hours. To maintain an increase in temperature of 3°C/min the furnace output is 25-28%. This corresponds to 600 to 650 W. To maintain a temperature of 400-500°C requires furnace output of 15-17% or 350 to 400 W. The total energy consumption for conventional regeneration of a 100 g sample of spent catalyst is between 2.9 and 3.2 kWh or 29-32 kWh/kg.

A number of fixed expenses and consumables are not included in this estimate. The costs incurred may not be determined until the configuration of the full scale system is determined. Some of the costs which must be determined are

enumerated below:

- capital cost of reactor and laser(s)
- maintenance and laser optics
- repair and replacement parts
- labour
- gas supply or compression
- material handling costs
- chemical and physical analysis

Upon scale-up significant changes in the nature of the processing may be required. The consumption of gases, for example, will vary depending on the nature of the agitation mechanism. The laser intensity and hence the power required will vary with the expected dwell time and the state of agitation of the particles in the laser radiation. Again, a significant amount of engineering and testing is required to determine the cost of constructing a laser regeneration unit for processing commercially significant quantities of catalyst.

Chapter 4

Conclusions and Recommendations

4.1 Conclusions

- The laser catalyst regeneration method has been used to clean and rejuvenate commercially spent catalyst extrudates. The chemical composition of the catalyst surface has been shown, by several analytical techniques, to be equivalent to conventionally regenerated material. Structural integrity of laser regenerated extrudates has been demonstrated by optical and electron microscopy, and by crush strength determination.

- For the coked hydrotreating extrudates examined here, the laser regeneration process requires multiple individual particle residence times, each of about 1s, and total integrated irradiation times of the order of a minute, an atmosphere enriched in oxygen (>20%), and intensities of about 50 W/cm^2.

- It is clear that the laser regeneration process is subject to strong mass-tranfer limitations. Due to this fact we believe that the laser regeneration process may be more readily modelled than the conventional process. The rates of reaction are much higher in the conventional method. Problems due to the intrinsic complexity of the chemistry of hydrotreating catalyst regeneration may be relieved.

- The energy efficiency of the laser regeneration unit has been shown to be competitive with that of the conventional unit. The estimated cost for laser regeneration using the current unit is about $1.50 /kg of spent hydrotreating catalyst.

4.2 Recommendations

- The only true test of the laser regeneration process is to use the samples in a HDS reactor. The laser regeneration method should be tested in this manner using laser rejuvenated samples in a bench scale reactor.

- Further characterization of laser regenerated materials to determine the impact of possible effects, such as selective ablation or attrition and intra-particle metals (Mo or Ni/Co) migration, should be performed. Regenerated extrudate sectioning and Auger or elecron microprobe analysis would provide this information.

- The possibility that laser processing may remove otherwise permanent poisons to catalyst activity should be investigated. Rapid laser heating may remove physical contaminants such as ash or heavy metals. Some chemical poisons such as sulphates appear to be more easily avoided or removed by laser regeneration.

- The state of dispersion of the active metal oxides on laser regenerated materials has not yet been determined. The relative positions of the MoO_3 crystallites and the promoters on the catalyst support is also unstudied. There may be interesting effects in these two areas due to the very different thermal history of laser regenerated materials.

Chapter 5

Summary

A bench-scale unit for laser processing of catalytic materials has been designed and constructed. The unit is capable of processing batches of commercial hydrotreating catalyst, sufficient to provide for semi-pilot plant reactor operation. The operation of the laser processing unit has been tested by laser regeneration of commercially spent hydrotreating catalyst material. A patent has been granted on this laser catalyst regeneration process.

Examination of laser regenerated extrudates has shown that their chemical and physical structure are equivalent to commercially regenerated materials. The analytical techniques used in this study include Proton Induced X-ray Emission (PIXE) elemental analysis, Fourier Transform Infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and crush strength analysis. The tests were all performed on oxidic catalyst material, but all indications are that once sulphided, the catalysts should regain their activity. The ultimate test of using laser regenerated materials in a hydrotreating reactor has yet to be performed.

Comparison has been made from the start of the laser processing work with conventional thermal processing. A state of the art furnace was designed and built to facilitate this comparison. Materials processed with this system served as a benchmark for the laser method. The chemical and physical properties of the laser processed materials compared favourably with conventionally processed materials.

Although a full economic evaluation of the possible commercial application of

the laser catalyst processing technology cannot yet be given, the energy efficiency of the bench-scale unit for laser regeneration has been shown to marginally more efficient than the bench-scale conventional unit. This is an encouraging sign that commercial exploitation of this novel technology may be possible.

References

Abbate, A.D., Kawai, T., Moore, C.B. and Chin, C-T., Surface Science, 136, L19, 1984

Bogdanor, J.M. and Rase, H.F., Ind. Eng. Prod. Res. Dev., 25, 220, 1986

Breysse, M., Bennett, B.A. and Chadwick, D., J. Catal., 71, 430, 1981

Brinen, J.S., Allard, L.F. and Daly, F.P., Surf. Interface Anal., 9, 227, 1986

Brinen, J.S., D'Avignon, D.A., Meyers, E.A., Deng, P.T. and Behnken, D.W., Surf. Interface Anal., 6(6), 295, 1984

Brinen, J.S., Graham, S.W., Hammond, J.S. and Paul, D.F., Surf. Interface Anal., 6(2), 68, 1984

Brown, J.R., Proceedings of 11^{th} International Conference on X-ray Optics and Micronalysis, London, Canada, 1986

Chianelli, R.R., Ruppert, A.F., Behal, S.K., Kear, B.H., Wold, A. and Kershaw, R., J. Catal., 92, 56, 1985

Chiu, N-S., Bauer, S.H. and M.F.L. Johnson, J. Catal., 98, 32, 1986

Clark, G.M. and Doyle, W.P., Spectrochim. Acta., 22, 1441, 1966

Daly, F.P., Brinen, J.S., Schmitt, J.L., Appl. Catal., 11, 161, 1984

Delmon, B., Surf. Interface Anal., 9, 195, 1986

Fransen, T., Van Der Meer, O. and Mars, P., J. Catal., 42, 79, 1976

Furimsky, E., Appl. Catal., 44, 189, 1988

Furimsky, E., Houle, J. and Yoshimura, Y., Appl. Catal., 33, 97, 1987

Furimsky, E., and Yoshimura, Y., in Handbook of Heat and Mass Transfer, Vol. 3, Kinetics, Catalysis and Reactor Eng., Gulf Publisher, Houston, TX, 1988

Gajardo, P., Grange, P. and Delmon, B., J. Catal., 63, 201, 1980

Harris, S. and Chianelli, R.R., J. Catal., 98, 17, 1986

Jepsen, J.S. and Rase, H.F., Ind. Eng. Prod. Res. Dev., 20, 467, 1981

Johnson, M.F.L., Voss, A.P., Bauer, S.H. and Chiu, N-S., J. Catal., 98, 51, 1986

Lipsch, J.M.J.G., and Schuit, G.C.A., J. Catal., 15, 163, 1969a

Lipsch, J.M.J.G., and Schuit, G.C.A., J. Catal., 15, 174, 1969b

Mitchell, P.C.H. and Trifiro, F., J. of Catal., 33, 350, 1974

Nyquist and Kagel, Infrared Spectra of Inorganic Compounds

Okotumi, M., Kasamatsu, K., Tsukamoto, K., Shiratori, S. and Uchiyama, F., Appl. Phys. Lett., 44(12), 1984

Ratnasamy, P., Knözinger, H., J. Catal., 54, 155, 1978

Ratnasamy, P., Ramaswamy, A.V., Banerjee, K., Sharma, D.K. and Ray, N., J. Catal., 38, 19, 1975

Robertson, J. and O'Reilly, E.P., Phys. Rev. B, 35, 2946, 1987

Sonnemans, J. and Mars, P., J. Catal., 31, 209, 1973

Taguchi, G., Systems of experimental design. Vol 1 (1976) and Vol 2 (1977), unipub/krauss international publications, white plains, New York .

Thakur. D.S. and Thomas. M.G.. Appl. Catal.. 15. 197. 1985

Tomoyuki. I.. Otawa. T.. Tsutchihashi. K. and Takegami. Y.. Carbon. 20(3). 213. 1982

Topsøe. H.. Clausen. B.S.. Candia. R.. Wivel. C. and Mørup. S.. J. Catal.. 68. 433. 1981

Topsøe. H.. Clausen. B.S.. Topsøe. N.Y. and Pederson. E.. Ind. Eng. Chem. Fundam. .25. 25. 1986

Topsøe. N.. J. Catal.. 64. 235. 1980

Weisz. P.B.. Chem. Eng. Progr. Symp. Ser.. 55. 29. 1959

Weisz. P.B.. and Goodwin. R.D.. J. Catal.. 2. 397. 1963

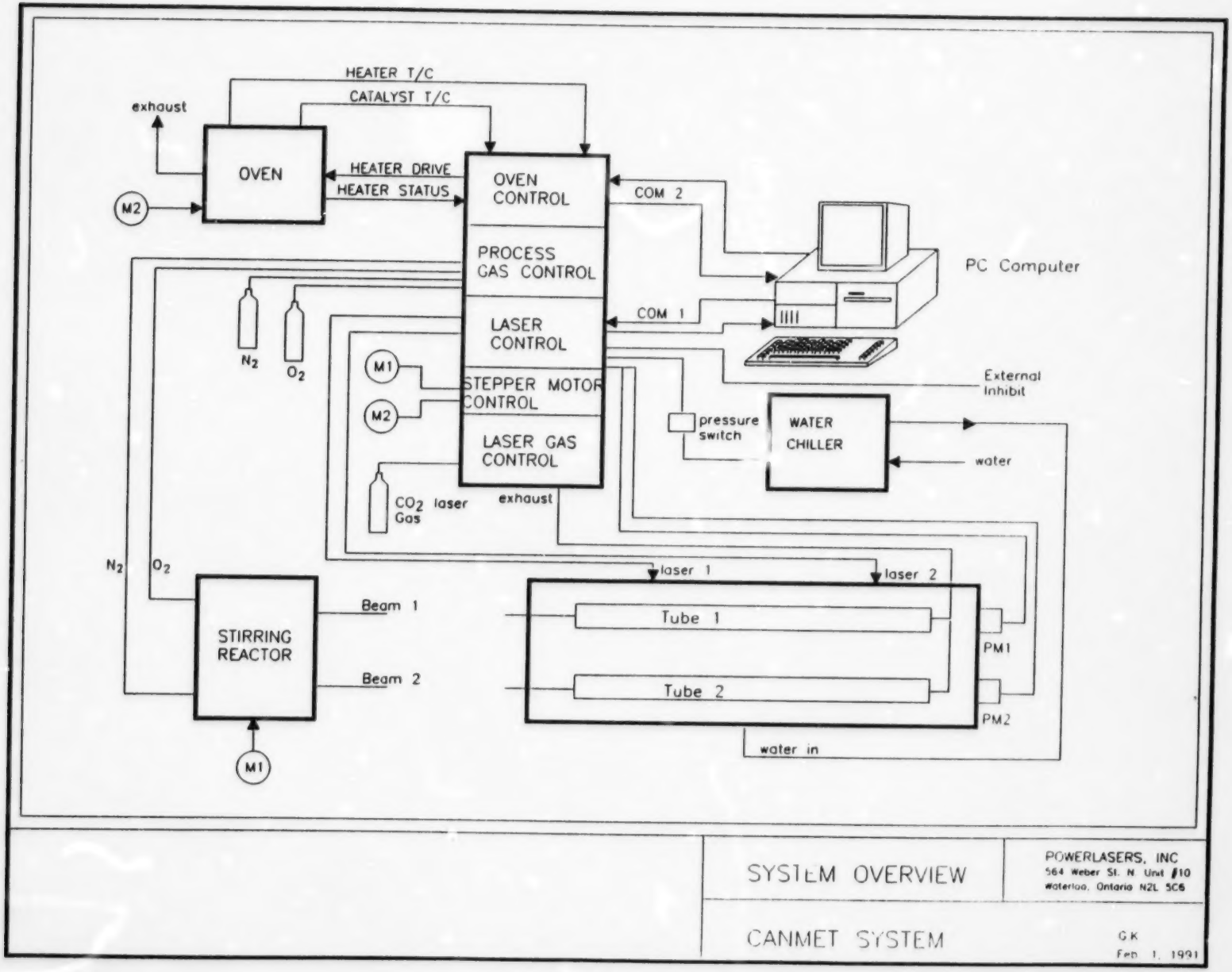
Wivel. C.. Candia. R.. Clausen. B.S.. Mørup. S.. and Topsøe. H.. J. Catal.. 68. 453. 1981

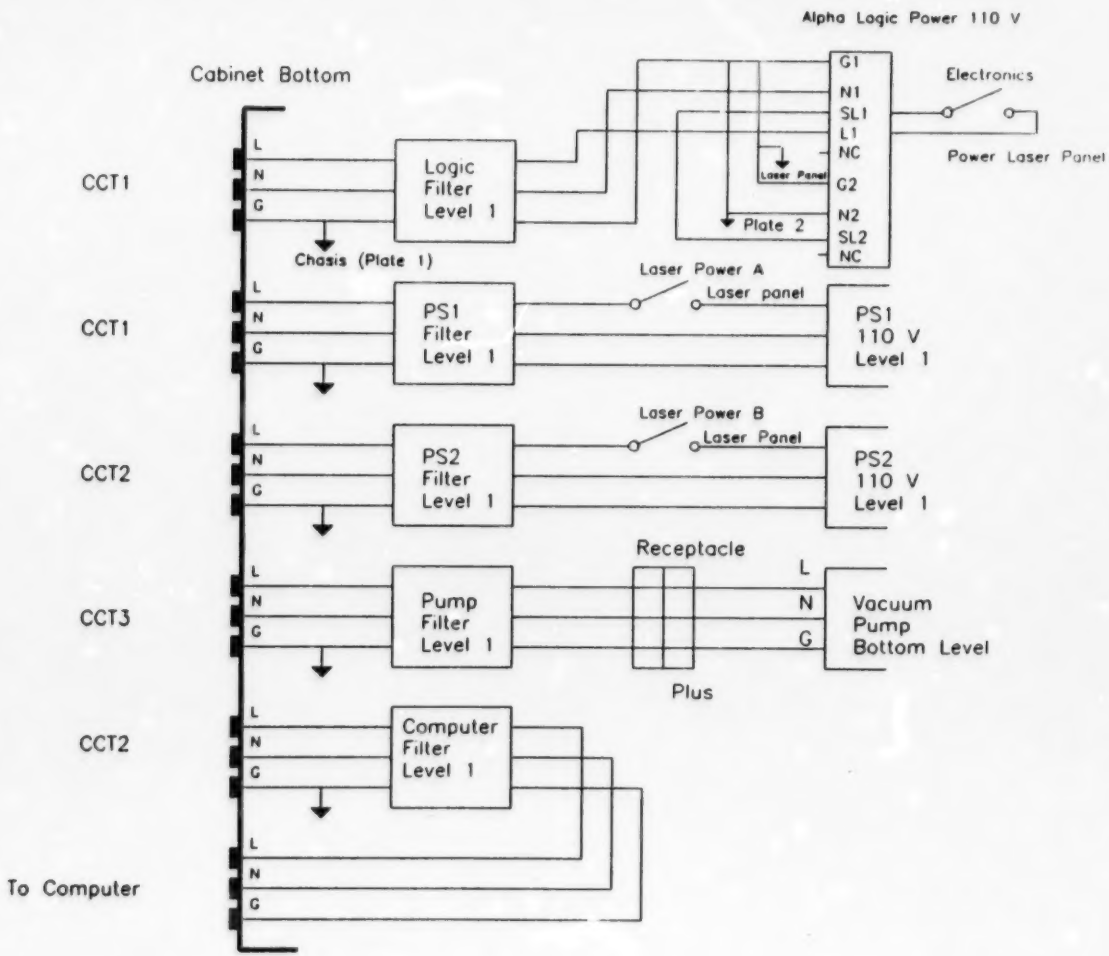
Wukasch. J.E.. Rase. H.F.. Ind. Eng. Chem. Prod. Dev.. 23. 558. 1982

Yoshimura. Y. and Furimsky. E.. App. Catal.. 23. 157. 1986

Appendix A

The following are drawings of the electronics for the laser and conventional catalyst processing systems.


HEATER T/C
CATALYST T/C
exhaust
OVEN
M2
HEATER DRIVE
HEATER STATUS
OVEN CONTROL
PROCESS GAS CONTROL
LASER CONTROL
STEPPER MOTOR CONTROL
LASER GAS CONTROL
COM 2
COM 1
PC Computer
N2
O2
M1
M2
External Inhibit
pressure switch
WATER CHILLER
water
CO2 Gas
laser
exhaust
N2
O2
laser 1
laser 2
STIRRING REACTOR
Beam 1
Beam 2
Tube 1
Tube 2
PM1
PM2
M1
water in
SYSTEM OVERVIEW
POWERLASERS, INC
564 Weber St. N. Unit #10
Waterloo, Ontario N2L 5C6
CANMET SYSTEM
GK
Feb 1, 1991

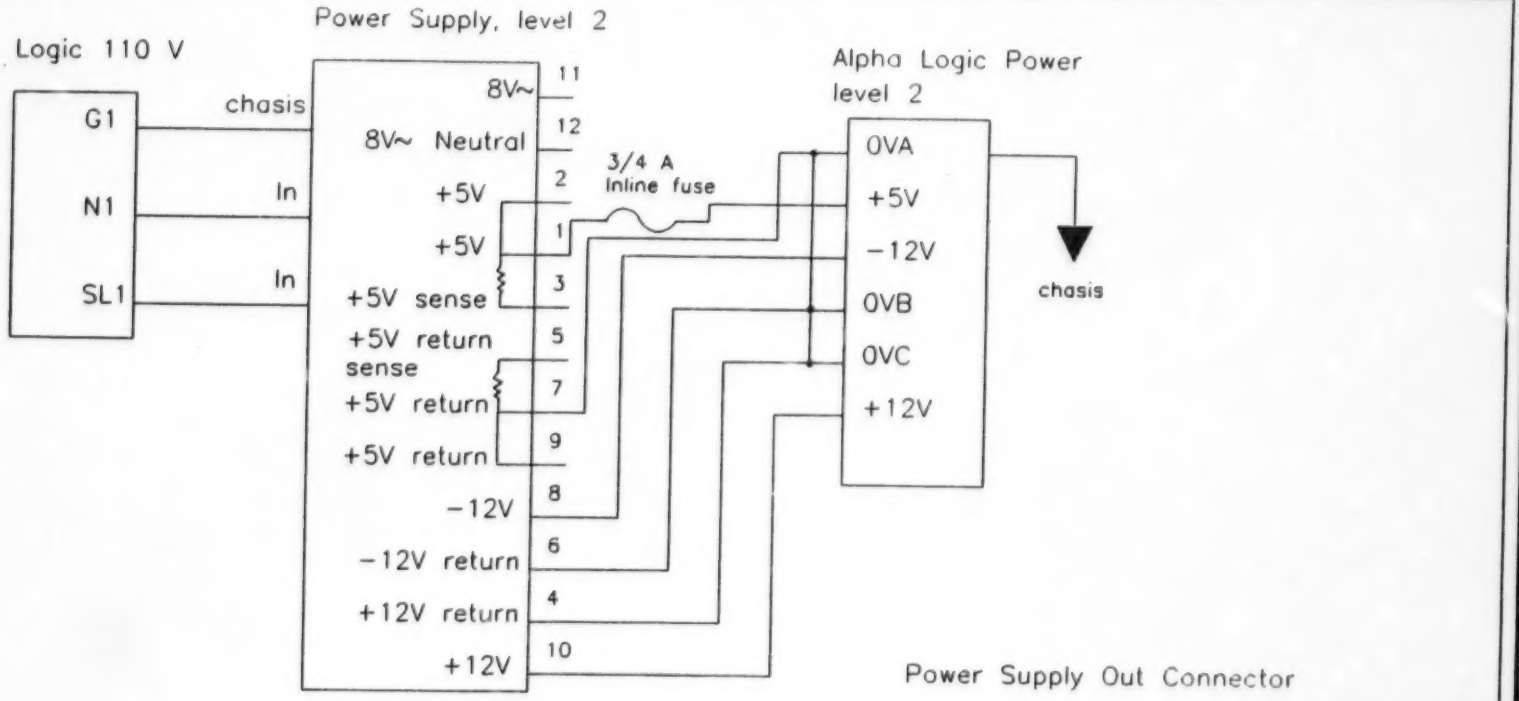


110 V Power Connections

POWERLASERS, INC
564 Weber St. N Unit #10
Waterloo, Ontario N2L 5C6

CANMET SYSTEM

G.K
Feb. 1, 1991



Power Supply Out Connector

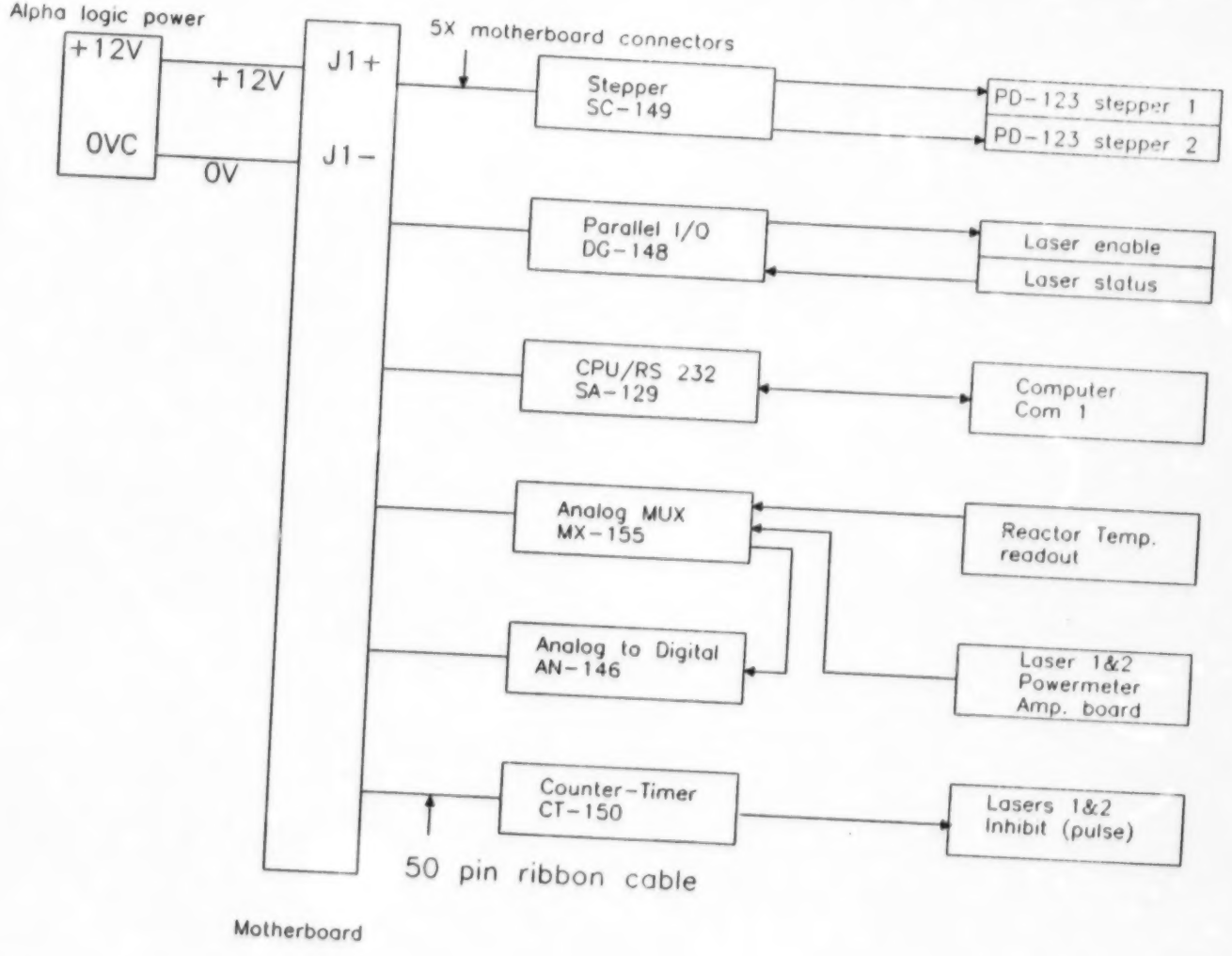
8V~ 11	o o	12	8V~ return
+5 return 9	o o	10	+12V
+5 return 7	o o	8	−12V
+5 return sense 5	o o	6	−12 return
+5 return 3	o o	4	+12 return
+5V 1	o o	2	+5V

Logic Power Supply Connections

POWERLASERS, INC
564 Weber St. N. Unit #10
Waterloo, Ontario N2L 5C6

CANMET SYSTEM

GK
Feb 1, 1991

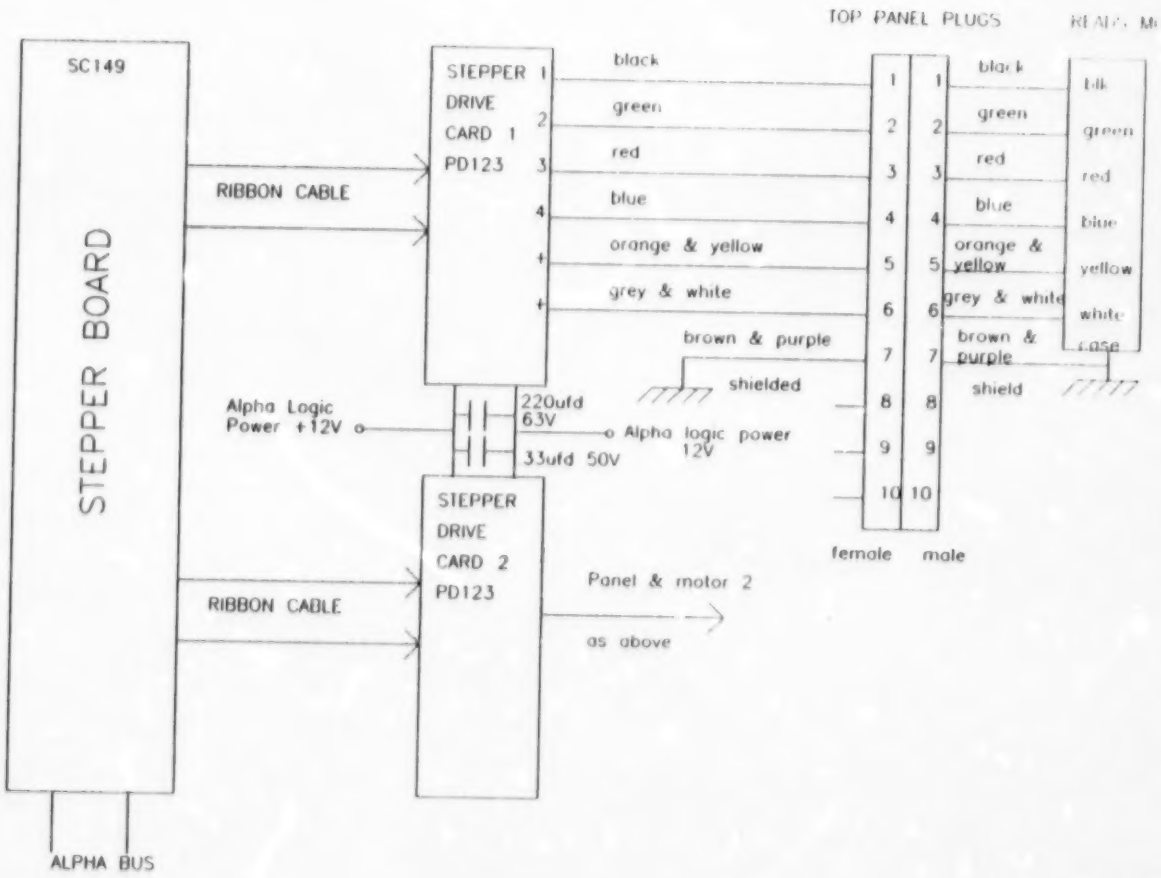


Alpha Bus
Connections

POWERLASERS, INC
564 Weber St. N Unit #10
Waterloo, Ontario N2L 5C6

CANMET SYSTEM

GK
Feb 1, 1991

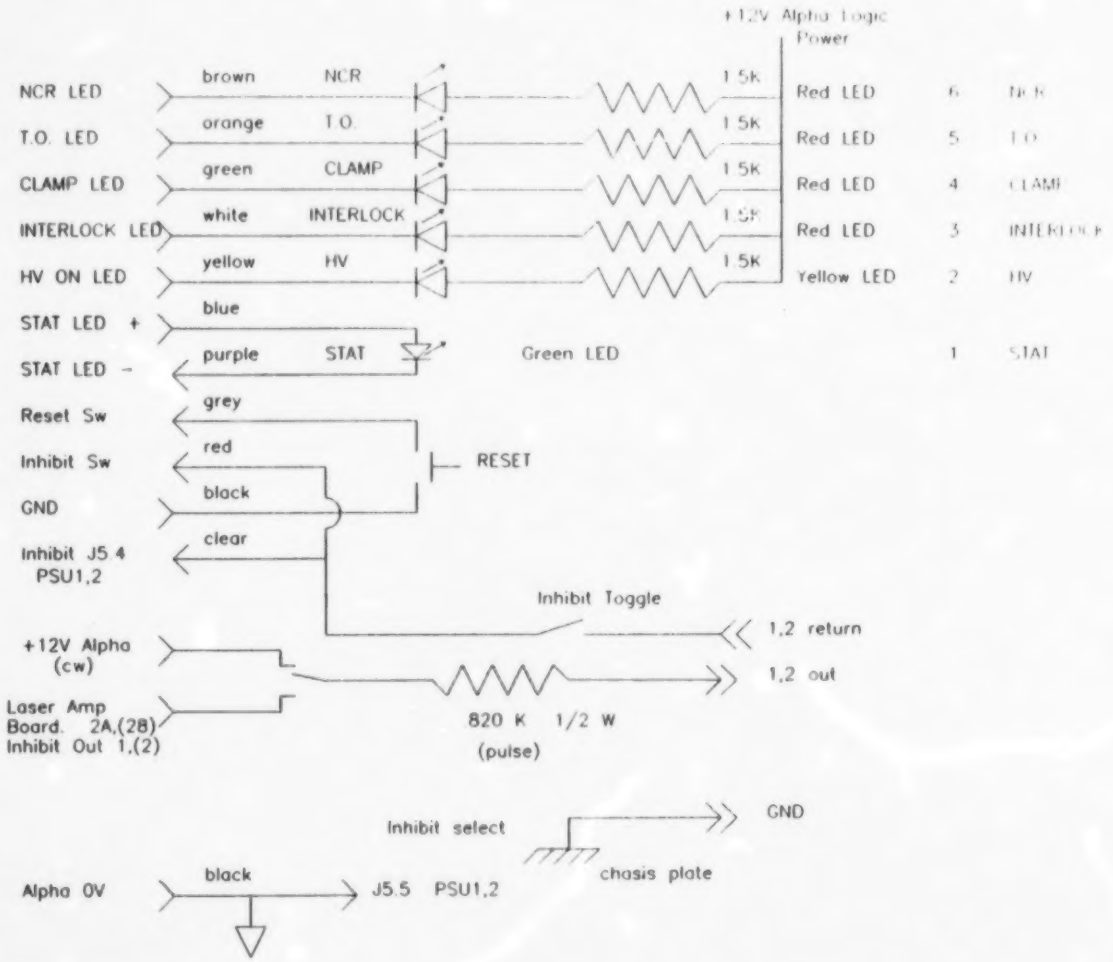


Alpha Bus
Stepper Drives

CANMET SYSTEM

POWERLASERS, INC
561 Weber St. N. Unit #10
Waterloo, Ontario N2L 5C6

G.K., K.B.
Feb. 1, 1991

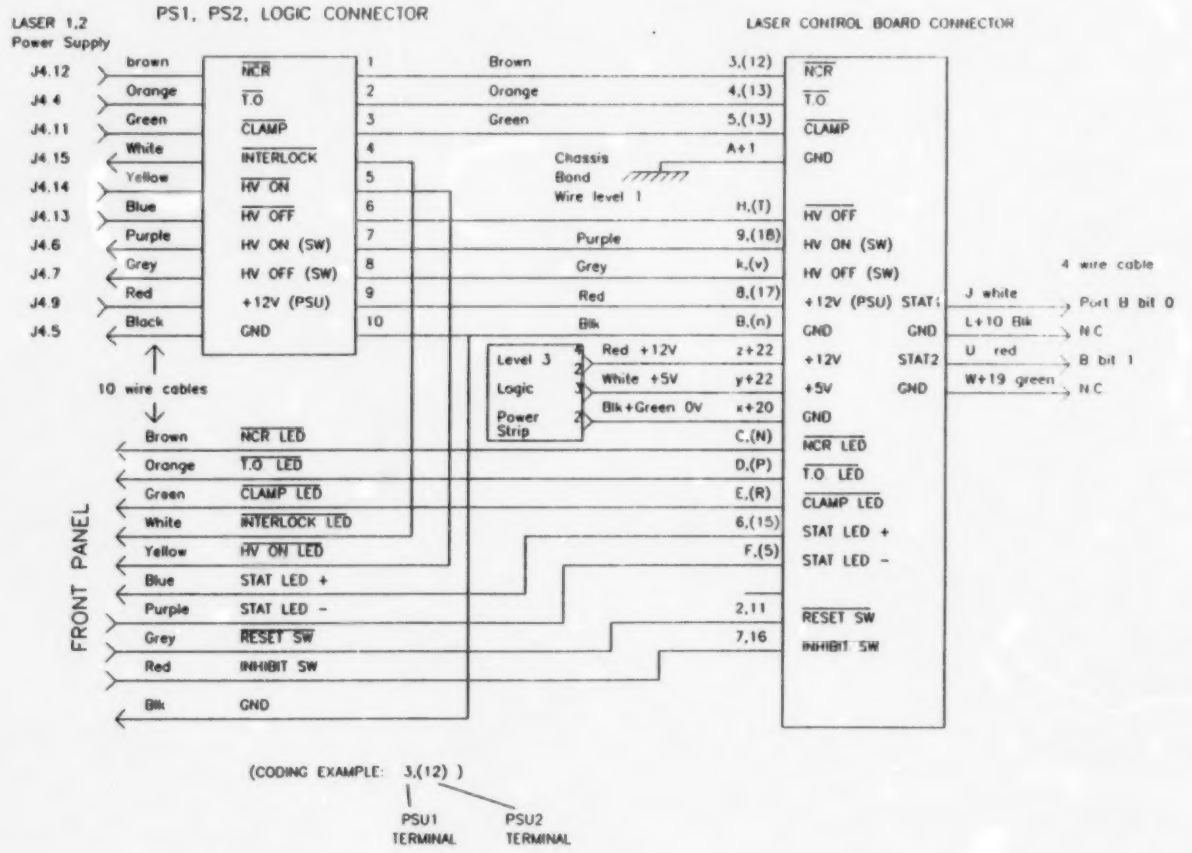


LASER PANEL WIRING

POWERLASERS, INC
564 Weber St N Unit #10
Waterloo, Ontario N2L 5C6

CANMET SYSTEM

G.K., K.B
Feb 1, 1991

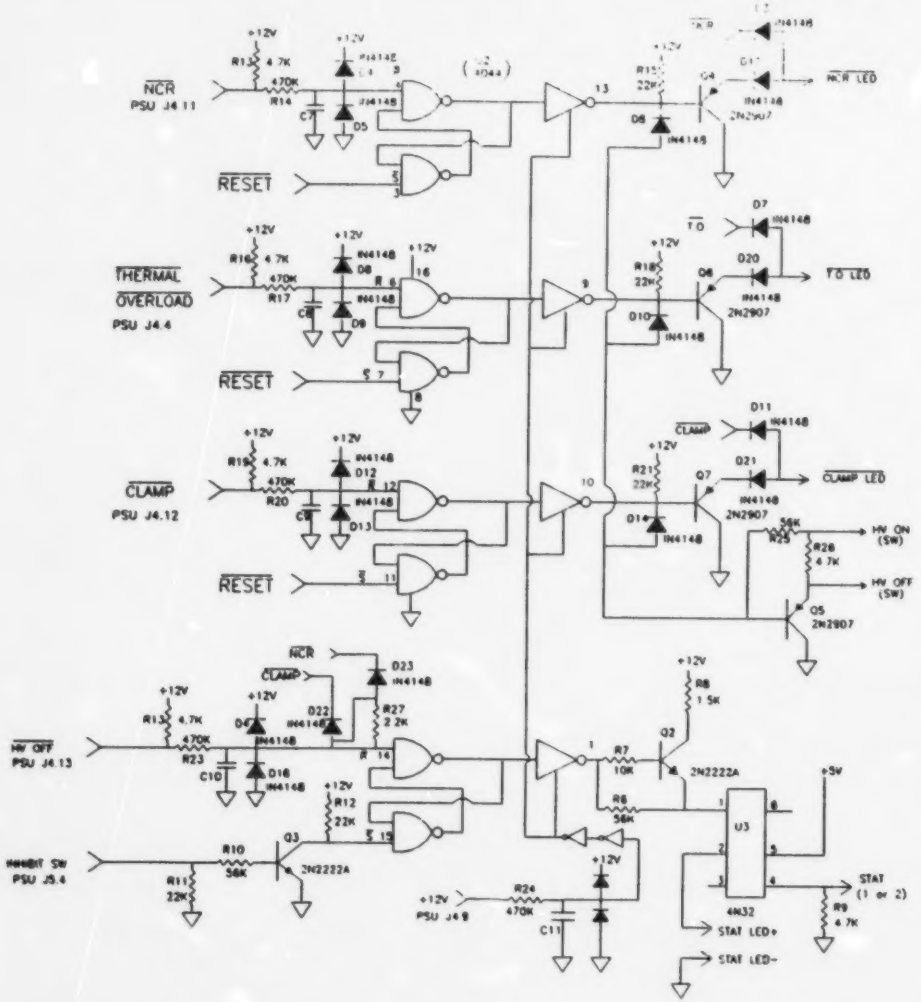


LASER CONTROL BOARD CONNECTIONS

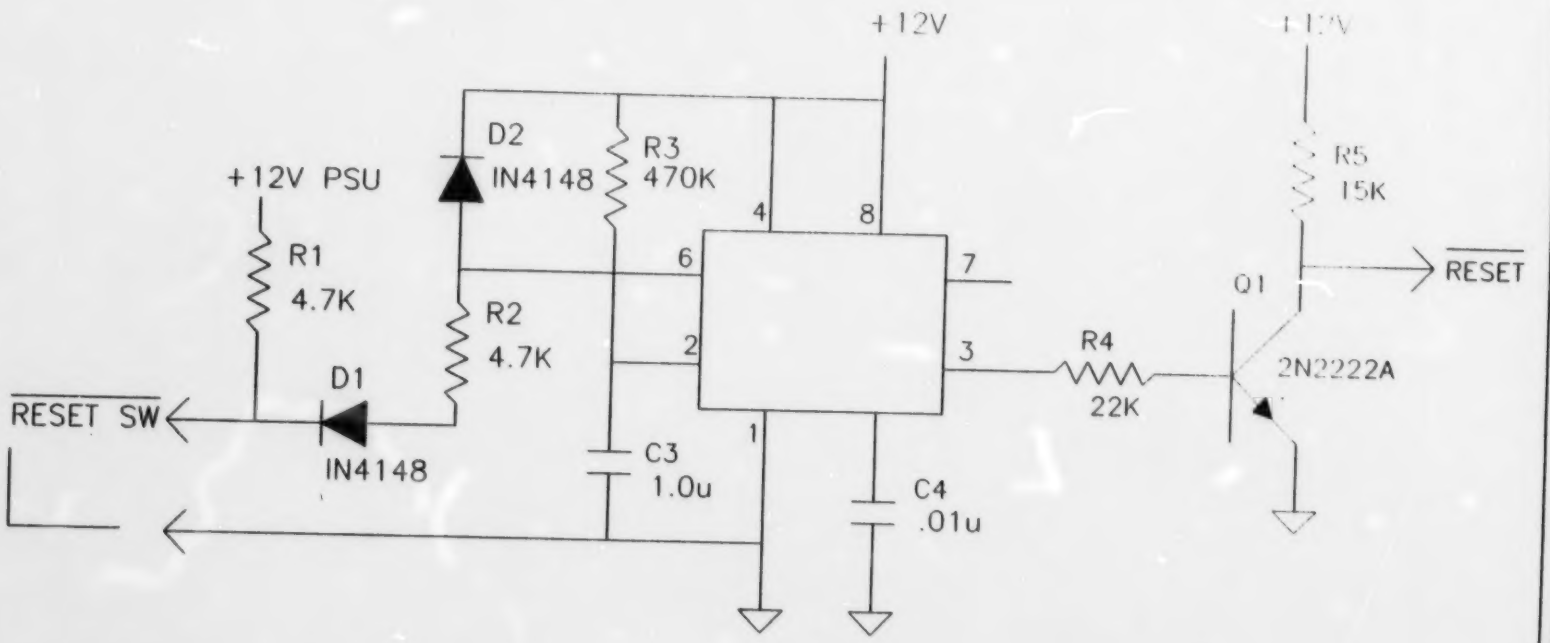
POWERLASERS, INC
164 Weber St. N. Unit #10
Waterloo, Ontario N2L 5C6

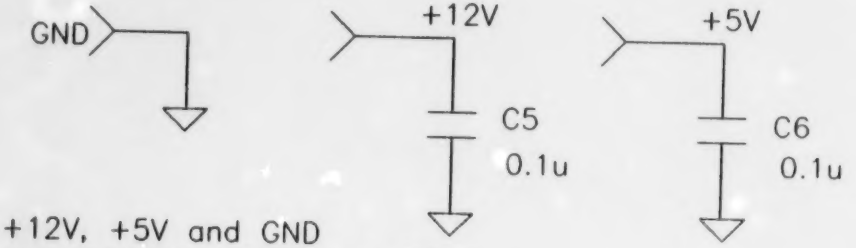
CANMET SYSTEM

G.K.
Feb. 1, 1991



	LASER CONTROL BOARD sheet A	POWERLASERS, INC 564 Weber St. N. Unit #10 Waterloo, Ontario N2L 5C6
	CANMET SYSTEM	G.F., K.B. Feb 1, 1991





+12V, +5V and GND
are common to PSU1 & PSU2

* C7, C8, C9 are removed to decrease the response time of the shutoff system.

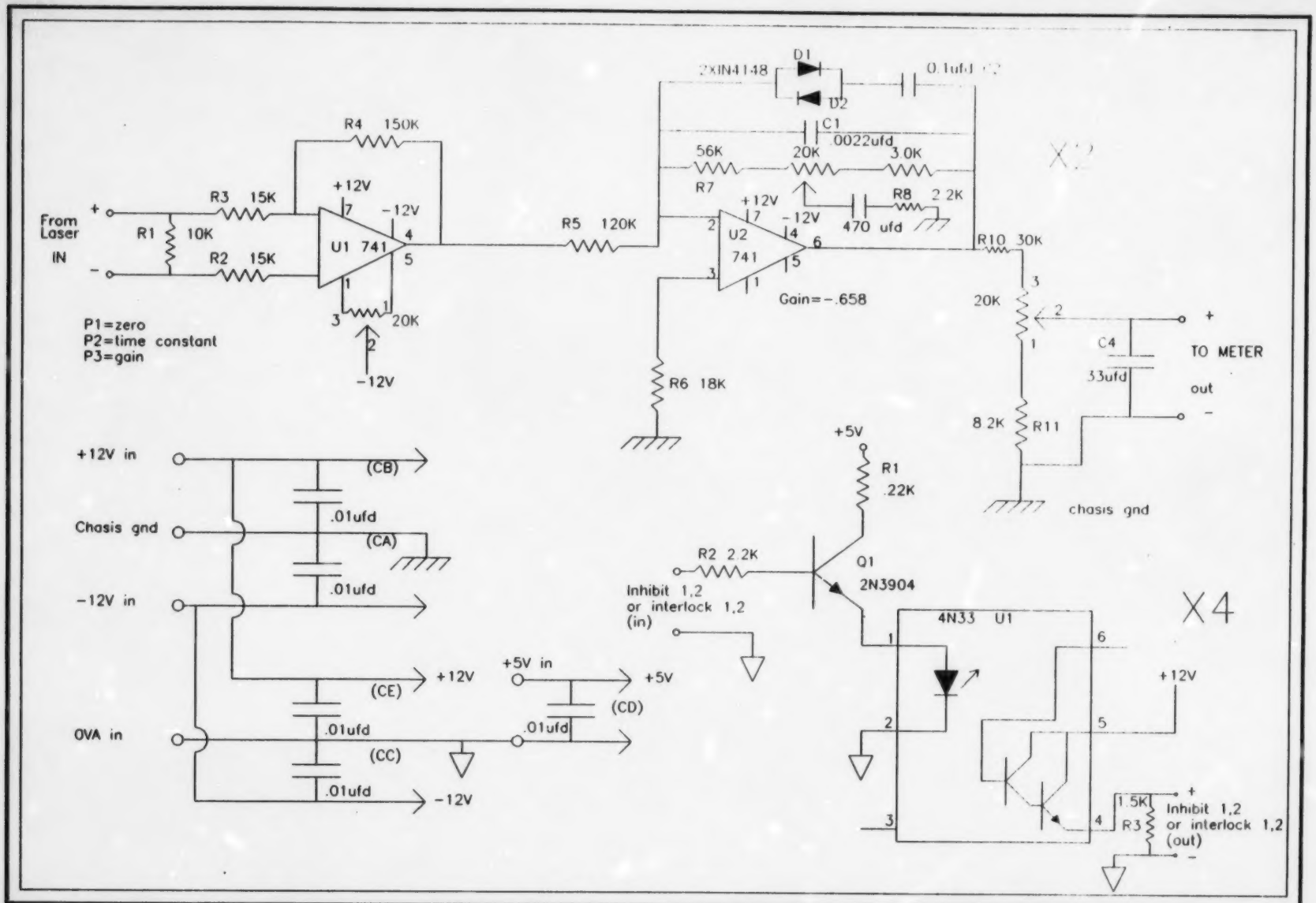
All components are duplicated from PSU1 to make the PSU2 circuit.

LASER CONTROL
BOARD sheet b

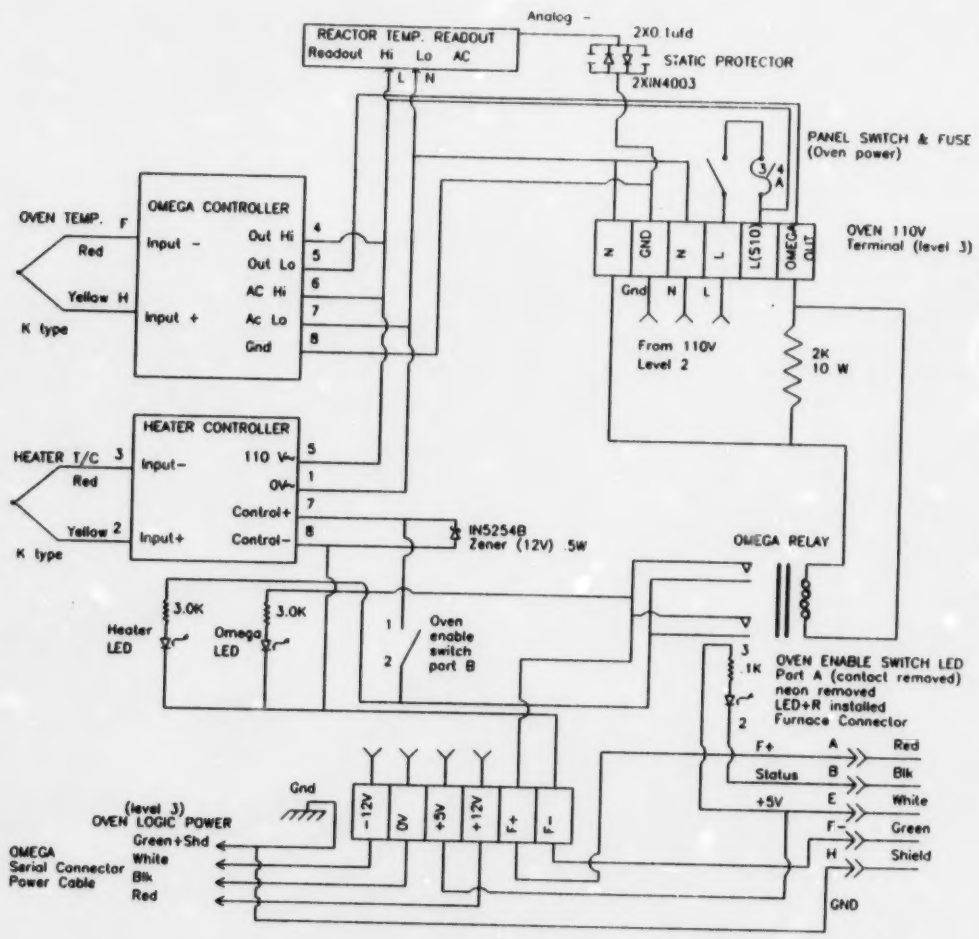
CANMET SYSTEM

POWERLASERS, INC
504 Weber St. N. Unit #10
Waterloo, Ontario N2L 5C6

G.K., K.B.
Feb. 1, 1991



	Laser Amp Board	POWERLASERS, INC 564 Weber St. N. Unit #10 Waterloo, Ontario N2L 5C6
	CANMET SYSTEM	G.K., K.B. Feb. 1, 1991



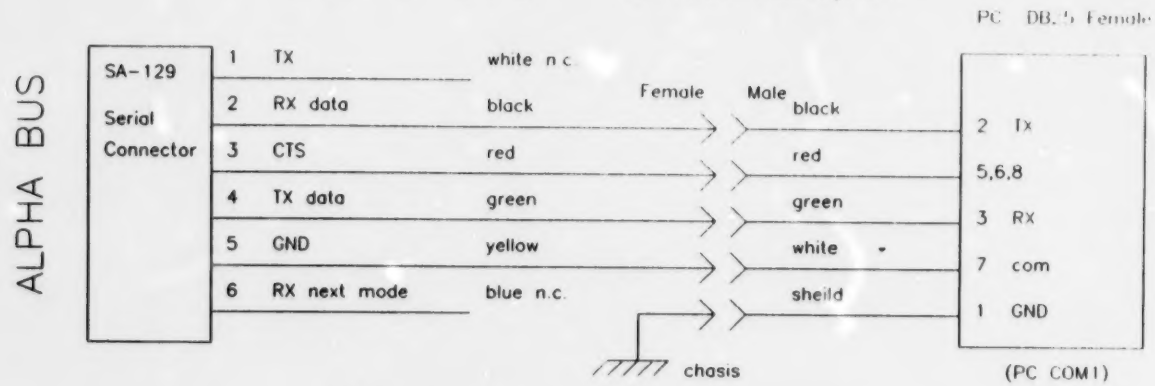
OVEN LOGIC WIRING

CANMET SYSTEM

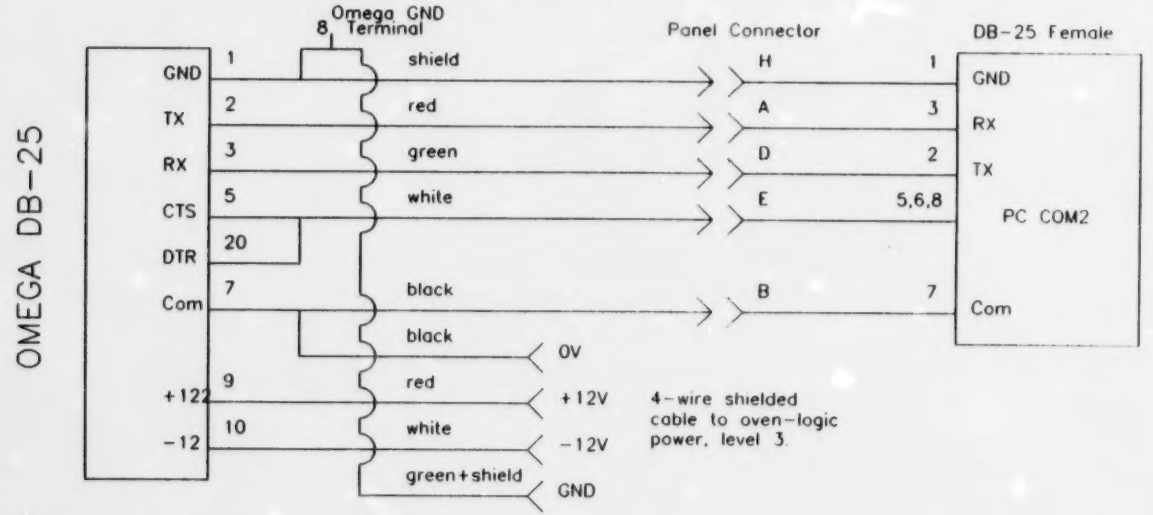
POWERLASERS, INC.
564 Weber St. N. Unit #10
Waterloo, Ontario N2L 5C6

G.K., K.B
Feb. 1, 1991

ALPHA BUS – Serial Adapter



OMEGA Serial Connections



	SERIAL CONNECTORS	POWERLASERS, INC 564 Weber St. N. Unit #10 Waterloo, Ontario N2L 5C6
	CANMET SYSTEM	G.K., K.B Feb. 1, 1991

Appendix B

The following pages contain a listing of the control and data acquisition software for the laser and conventional catalyst processing units.

```
'    LASER.BAS  WRITTEN BY K. BRUNDRETT
'    LAST MODIFIED   MAR 8, 91
'
DECLARE FUNCTION RPM! (STEPS!)
DECLARE SUB OOFF ()
DECLARE SUB STEPPER (SPEED!, MOTOR$)
DECLARE SUB OCOLLECT ()
DECLARE SUB REACTORSET ()
DECLARE SUB DATAFILENAME (DFILE$, FILENO!)
DECLARE SUB RCOLLECT ()
DECLARE FUNCTION MVREAD! (CHANNEL%)
DECLARE FUNCTION HSTRTOI% (HSTR$)
DECLARE SUB TWAIT (COUNTS%)
DECLARE SUB ADTEST ()
DECLARE SUB OPENOMEGA ()
DECLARE FUNCTION GETRM2$ ()
DECLARE FUNCTION FSTR$ (DP!, NUM AS LONG)
DECLARE FUNCTION PSTR$ (DP!, NUM AS LONG, PWB2 AS LONG)
DECLARE SUB LOFF (LASER$)
DECLARE SUB TRIGGER (LASER$)
DECLARE SUB ENABLE ()
DECLARE SUB PULSESET ()
DECLARE FUNCTION GETRM1$ ()
DECLARE SUB LASERMENU ()
DECLARE SUB TIMERINIT ()
DECLARE SUB CONFIGMENU ()
DECLARE SUB OVENSET ()
DECLARE SUB OPENALPHA ()
DECLARE SUB MENU (MENUNAME$, MENUCHOICES$(), NUMCHOSEN%)
DECLARE SUB FRAME (LEFTCOL%, RIGHTCOL%, TOPROW%, BOTTOMROW%)
DECLARE SUB CONFIGDATAFILE (CMODE$)
DECLARE SUB DELAY (TME!)
DECLARE FUNCTION YESNO! (PROMPT$)
DECLARE FUNCTION DIFF! (TIM!)
DECLARE SUB ATERM ()
DECLARE SUB OTERM ()
DECLARE SUB LASERON (LASER$)
DECLARE SUB ROFF ()
'
'
'--------------------[  GLOBAL VARIABLE DECLARITIONS  ]-----------------------
'
' set the lowest subscript of all arrays to 1
'
        OPTION BASE 1
'
        COMMON SHARED TRUE%, FALSE%
        COMMON SHARED CFILE$
        COMMON SHARED RFILE$, RLENGTH%, RINT%, RSTEP, RSETFLAG%, RNAMEFLAG%
        COMMON SHARED OFILE$, OLENGTH%, OINT%, OSTEP, OSETFLAG%, ONAMEFLAG%
        COMMON SHARED RFILENO, OFILENO
        COMMON SHARED USERFLAG%
        COMMON SHARED DEBUGFLAG%
        COMMON SHARED QFLAG%
        COMMON SHARED ECHECK%
        COMMON SHARED RTRIG1$, RTRIG2$, ENAB1$, ENAB2$
        COMMON SHARED PRP AS LONG, PW1 AS LONG, PW2 AS LONG
        COMMON SHARED TBASE
'
'-------------------[  SET CONSTANTS AND FLAGS  ]-----------------------------
'
        TRUE% = -1   'Set boolean variables true% and false%
        FALSE% = 0
        RNAMEFLAG% = FALSE% 'Flag to indicate if the reactor file is set
        ONAMEFLAG% = FALSE% 'Flag to indicate if the oven file is set
'
'
'----------------------[  ARRAY DEFINITIONS  ]-------------------------------
'
        DIM MENUS$(3), MENU1$(9), MENU2$(6)
'
'---------------------[  MAIN PROGRAM AREA  ]-------------------------------
'
REINIT:
        QFLAG% = FALSE%
'
'
' read in the configuration data
'
        CALL CONFIGDATAFILE("READ")
```

```
'
' check for experienced users
'
'
SSTART:

        MENUSNAM$ = "CO2 LASER SYSTEM USER OPTIONS"
        MENUS$(1) = "E Expert, minimal prompting"
        MENUS$(2) = "D Debug, debug printing"
        MENUS$(3) = "N Normal, normal prompting"

        CHOICES% = 0
        CLS
        CALL MENU(MENUSNAM$, MENUS$(), CHOICES%)
        IF CHOICES% = 1 THEN
           USERFLAG% = FALSE%
           DEBUGFLAG% = FALSE%
           GOTO MSTART
        END IF
        IF CHOICES% = 2 THEN
           DEBUGFLAG% = TRUE%
           USERFLAG% = TRUE%
           GOTO MSTART
        END IF
        USERFLAG% = TRUE%
        DEBUGFLAG% = FALSE%
MSTART:
' OPEN THE ALPHA BUS
'
        CALL OPENALPHA
'       INITIALIZE THE CT-150 REGISTERS
        CALL TIMERINIT
        CALL OPENOMEGA
'
' define the strings for the main menu
'
        MENU1NAM$ = "SYSTEM SETUP MENU"
        MENU1$(1) = "1 Laser control and start"
        MENU1$(2) = "2 Set the reactor parameters"
        MENU1$(3) = "3 Set the oven parameters"
        MENU1$(4) = "4 Save or load the configuration"
        MENU1$(5) = "5 Enter ALPHA terminal mode"
        MENU1$(6) = "6 Enter OMEGA terminal mode"
        MENU1$(7) = "7 Enter A/D test"
        MENU1$(8) = "8 Enter experiment control menu"
        MENU1$(9) = "q quit"
'
' start by displaying the main line menu
'
MAINMENU:
        CHOICE1% = 0
        WHILE CHOICE1% <> 9
                CLS
                CALL MENU(MENU1NAM$, MENU1$(), CHOICE1%)
                IF CHOICE1% = 1 THEN CALL LASERMENU
                IF CHOICE1% = 2 THEN CALL REACTORSET
                IF CHOICE1% = 3 THEN CALL OVENSET
                IF CHOICE1% = 4 THEN CALL CONFIGMENU
                IF CHOICE1% = 5 THEN CALL ATERM
                IF CHOICE1% = 6 THEN CALL OTERM
                IF CHOICE1% = 7 THEN CALL ADTEST
                IF CHOICE1% = 8 THEN GOTO RUNEXP
        WEND
        GOTO QUIT
'
'
RUNEXP:
        IF USERFLAG% = TRUE% THEN
          CLS : PRINT "THIS SPACE IS RESERVED FOR THE EXPERIMENT SETUP MESSAGE"
          PRINT : PRINT : DO: LOOP UNTIL INKEY$ = "": INPUT "Press return to continue"; ANS$
        END IF
'
'
'
' This part of the program contains the experiment menu
'
'
' set up the menu for running the experiment
'
        MENU2NAM$ = "MENU TO CONTROL THE EXPERIMENT"
        MENU2$(1) = "1  Laser control and start"
```

```
        MENU2$(2) = "2  Collect reactor data"
        MENU2$(3) = "3  Collect oven data"
        MENU2$(4) = "4  Enter ALPHA terminal mode"
        MENU2$(5) = "5  Enter OMEGA terminal mode"
        MENU2$(6) = "r  return to the main menu"
'
        CHOICE2% = 0
        WHILE CHOICE2% <> 6
           NAMEFLAG% = FALSE%
           CLS
           CALL MENU(MENU2NAM$, MENU2$(), CHOICE2%)
           IF CHOICE2% = 1 THEN CALL LASERMENU
           IF CHOICE2% = 2 THEN CALL RCOLLECT
           IF CHOICE2% = 3 THEN CALL OCOLLECT
           IF CHOICE2% = 4 THEN CALL ATERM
           IF CHOICE2% = 5 THEN CALL OTERM
        WEND
        GOTO MAINMENU
'
'
QUIT:
        CALL ROFF
        CALL OOFF
        CLS : PRINT
        QFLAG% = TRUE%
        PRINT : QUESTION = YESNO("Do you want to save the configuration data?")
        IF QUESTION = TRUE% THEN CALL CONFIGDATAFILE("WRITE")
        PRINT : QUESTION = YESNO("QUIT ?")
        IF QUESTION = FALSE% THEN
            QFLAG% = FALSE%
            GOTO SSTART
        END IF
'
        END
'
' ERROR TRAPPING FOR ALPHA OPENING
'
ERTRAP: PRINT : PRINT "SYSTEM ERROR IN ALPHA OPENING"
        PRINT "STARTING AGAIN"
        CLOSE #1
        RESET
        CALL DELAY(2)
        RESUME REINIT
'
' ERROR TRAPPING FOR ALPHA OPENING
'
OERTRAP: PRINT : PRINT "SYSTEM ERROR IN OMEGA OPENING"
        PRINT "STARTING AGAIN"
        CLOSE #1
        CLOSE #2
        RESET
        CALL DELAY(2)
        RESUME REINIT
'
'
'               IF THIS TEST FAILED THEN FILE DID NOT EXIST
'
OPENERROR:      ECHECK% = TRUE%
                RESUME NEXT
'
'
'
TTRAP:
                CALL LOFF("BOTH")
                ENAB1$ = "N"
                ENAB2$ = "N"
                CALL ENABLE
                PRINT : PRINT "FATAL ERROR IN PROCESSING - EXITING"
                QFLAG% = TRUE%
                PRINT : QUESTION = YESNO("Do you want to save the configuration data?")
                IF QUESTION = TRUE% THEN CALL CONFIGDATAFILE("WRITE")
                END
'
'*************************[  SUBROUTINE AREA  ]*********************************
'
'

        SUB ADTEST

        PRINT "Q WILL EXIT WHEN DONE"
        INPUT "ENTER THE DESIRED SELECTION FOR THE MUX BOARD"; CHANNEL%
```

```
        DO WHILE UCASE$(ANS$) <> "Q"
        PRINT "CHANNEL "; CHANNEL%; " READS "; MVREAD(CHANNEL%); " mV."
        ANS$ = INKEY$
        LOOP

        END SUB

        SUB ATERM
        PRINT "ENTERING ALPHA TERMINAL MODE (esc) KEY QUITS."
        ON ERROR GOTO TTRAP
        A$ = ""
        QUITS$ = CHR$(27)
        DO

          A$ = INKEY$
          IF A$ = QUITS$ THEN
                EXIT DO
          ELSEIF A$ <> "" THEN
                PRINT #1, A$;
                PRINT A$;
          END IF
          IF LOC(1) THEN
                PRINT INPUT$(LOC(1), #1);
          END IF
        LOOP
        PRINT #1, CHR$(3)
        ANS$ = GETRM1$
        END SUB

'
'-------------------------------------------------------------------------------
' SUBROUTINE to obtain the configuration data file name
'-------------------------------------------------------------------------------
'
        SUB CONFIGDATAFILE (CMODE$) STATIC
        CLS
        ON ERROR GOTO OPENERROR
        FILENO = FREEFILE
        IF CMODE$ = "READ" THEN
CREDO:      PRINT "Reading from existent configuration data file"
            QUESTION = YESNO("DO YOU WISH TO USE THE DEFAULT FILENAME")
            ECHECK% = FALSE%
            IF QUESTION = TRUE% THEN
                CFILE$ = "C:\LASER\CONFIG.LSR"
            ELSE
                DO: LOOP UNTIL INKEY$ = "": INPUT "What is the complete config data file name"; CFILE$
                IF CFILE$ = "" THEN
                    PRINT "CAN NOT USE A BLANK FOR A DATA FILE"
                    GOTO CREDO
                END IF
                CFILE$ = UCASE$(CFILE$)

            END IF
CREAD:      OPEN CFILE$ FOR INPUT AS #FILENO
            IF ECHECK% = TRUE% THEN
                PRINT "FILE  "; CFILE$; "  DOES NOT EXIST"
                GOTO CREDO
            END IF
            INPUT #FILENO, CONFIG$
            IF CONFIG$ <> "CONFIG" THEN
                PRINT "SPECIFIED FILE IS NOT A VALID CONFIGURATION FILE"
                PRINT "IF IT IS AN OLD CONFIG FILE THEN ADD FIRST AND LAST"
                PRINT "LINES AS SEEN IN C:\LASER\CONFIG.LSR"
                CLOSE #FILENO
                GOTO CREDO
            END IF
            INPUT #FILENO, PRP
            INPUT #FILENO, PW1
            INPUT #FILENO, PW2
            INPUT #FILENO, RTRIG1$
            INPUT #FILENO, RTRIG2$
            INPUT #FILENO, RLENGTH%
            INPUT #FILENO, RINT%
            INPUT #FILENO, RSTEP
            INPUT #FILENO, OLENGTH%
            INPUT #FILENO, OINT%
            INPUT #FILENO, OSTEP
            INPUT #FILENO, CONFIG$
            IF CONFIG$ <> "CONFIGEND" THEN
                PRINT "SPECIFIED FILE IS NOT A VALID CONFIGURATION FILE"
                PRINT "IF IT IS AN OLD CONFIG FILE THEN ADD FIRST AND LAST"
```

```
            PRINT "LINES AS SEEN IN C:\LASER\CONFIG.LSR"
            CLOSE #FILENO
            GOTO CREDO
        END IF
        CLOSE #FILENO

        RFILE$ = ""
        RNAMEFLAG% = FALSE%
        RSETFLAG% = FALSE%
        OFILE$ = ""
        ONAMEFLAG% = FALSE%
        OSETFLAG% = FALSE%

    ELSEIF CMODE$ = "WRITE" THEN
WCREDO:
        ECHECK% = FALSE%
        PRINT "Current configuration file is "; CFILE$
        QUESTION = YESNO("Do you want to update this config file")
        IF QUESTION = FALSE% THEN
            QUESTION = YESNO("Do you want to update the default config file")
            IF QUESTION = TRUE% THEN
                CFILE$ = "C:\LASER\CONFIG.LSR"
                GOTO WCONFIG
            END IF
            DO: LOOP UNTIL INKEY$ = "": INPUT "What is the complete config data file name"; CFILE$
            IF CFILE$ = "" THEN
                PRINT "CAN NOT USE A BLANK FOR A DATA FILE"
                GOTO WCREDO
            END IF
            CFILE$ = UCASE$(CFILE$)
            OPEN CFILE$ FOR INPUT AS #FILENO
            IF ECHECK% = FALSE% THEN
                 CLOSE #FILENO
                 PRINT
                 PRINT "File  "; CFILE$; "  already in existance"
                 PRINT
                 QUESTION = YESNO("Do you wish to over-write this")
                 IF QUESTION = FALSE% THEN GOTO WCREDO
            END IF
        END IF
WCONFIG:
        OPEN CFILE$ FOR OUTPUT AS #FILENO
        PRINT #FILENO, "CONFIG"
        PRINT #FILENO, PRP
        PRINT #FILENO, PW1
        PRINT #FILENO, PW2
        PRINT #FILENO, RTRIG1$
        PRINT #FILENO, RTRIG2$
        PRINT #FILENO, RLENGTH%
        PRINT #FILENO, RINT%
        PRINT #FILENO, RSTEP
        PRINT #FILENO, OLENGTH%
        PRINT #FILENO, OINT%
        PRINT #FILENO, OSTEP
        PRINT #FILENO, "CONFIGEND"
        CLOSE #FILENO
        PRINT : DO: LOOP UNTIL INKEY$ = "": INPUT "Press return to continue"; ANS$

    END IF
    IF QFLAG% = FALSE% THEN
        ON ERROR GOTO 0
    END IF
    END SUB

    SUB CONFIGMENU
'
    DIM CMENUS(3)
    CMENUNAM$ = "LASER DATA ACQUISTION"
    CMENUS(1) = "S Save the configuration file"
    CMENUS(2) = "L Load an existing configuration file"
    CMENUS(3) = "R Return to the main menu"
'
'
    CCHOICE% = 0
    WHILE CCHOICE% <> 3
            CLS
            CALL MENU(CMENUNAM$, CMENUS(), CCHOICE%)
            IF CCHOICE% = 1 THEN CALL CONFIGDATAFILE("WRITE")
            IF CCHOICE% = 2 THEN CALL CONFIGDATAFILE("READ")
    WEND

    END SUB
```

```
'
'-------------------------------------------------------------------------------
' SUBROUTINE to obtain the data file name
'-------------------------------------------------------------------------------
'
        SUB DATAFILENAME (DFILE$, FILENO) STATIC
        FILENO = FREEFILE
        ON ERROR GOTO OPENERROR
        APPENFLAG = FALSE%
        PRINT "ROUTINE TO OBTAIN THE DATA FILE NAME"
        PRINT "************************************"
        PRINT
REDO:   ECHECK% = FALSE%
        DO: LOOP UNTIL INKEY$ = "": INPUT "What is the complete data file name"; DFILE$
        IF DFILE$ = "" THEN
          PRINT "CAN NOT USE A BLANK FOR A DATA FILE"
          GOTO REDO
        END IF
        DFILE$ = UCASE$(DFILE$)
        OPEN DFILE$ FOR INPUT AS #FILENO
        IF ECHECK% = FALSE% THEN
            CLOSE #FILENO
            PRINT
            PRINT "This file already exists on the disk"
            PRINT : PRINT
            QUESTION = YESNO("DO YOU WANT TO APPEND TO THIS DATA FILE")
            IF QUESTION = TRUE% THEN
              OPEN DFILE$ FOR APPEND AS #FILENO
              GOTO FDONE
            ELSE
              QUESTION = YESNO("DO YOU WANT TO WRITE OVER THIS DATA FILE")
              IF QUESTION = TRUE% THEN
                QUESTION = YESNO("ARE YOU SURE YOU WANT TO WRITE OVER THIS DATA FILE")
                IF QUESTION = TRUE% THEN
                  GOTO FOPEN
                ELSE
                  GOTO REDO
                END IF
              ELSE
                PRINT
                PRINT "Please input a new file name"
                PRINT
                GOTO REDO
              END IF
            END IF
        END IF
FOPEN:
        OPEN DFILE$ FOR OUTPUT AS #FILENO
        PRINT : PRINT "The next 5 lines can be used to describe the experiment."
        PRINT "Hitting RETURN will result in blank lines.": PRINT
        DO: LOOP UNTIL INKEY$ = "": LINE INPUT "First line  :"; L1$
        DO: LOOP UNTIL INKEY$ = "": LINE INPUT "Second line :"; L2$
        DO: LOOP UNTIL INKEY$ = "": LINE INPUT "Third line  :"; L3$
        DO: LOOP UNTIL INKEY$ = "": LINE INPUT "Fourth line :"; L4$
        DO: LOOP UNTIL INKEY$ = "": LINE INPUT "Fifth line  :"; L5$
        PRINT #FILENO, DATE$; ",,"; "DATE OF TEST"
        PRINT #FILENO, TIME$; ",,"; "TIME OF TEST"
        PRINT #FILENO,
        PRINT #FILENO, L1$
        PRINT #FILENO, L2$
        PRINT #FILENO, L3$
        PRINT #FILENO, L4$
        PRINT #FILENO, L5$
        PRINT #FILENO,
        PRINT #FILENO,
FDONE:  ON ERROR GOTO 0
        END SUB

'
'-------------------------------------------------------------------------------
' SUBROUTINE TO PREFORM TIMER DELAY IN SOFTWARE
'-------------------------------------------------------------------------------
'
        SUB DELAY (TME) STATIC

'       DELAY FOR THE SECONDS
'
        T = TIMER: WHILE (DIFF(T)) < TME: WEND
        END SUB

'
```

```
'--------------------------------------------------------------------------------
' FUNCTION to correct for midnight using timer function
'--------------------------------------------------------------------------------
'
        FUNCTION DIFF (TIM)
'
'
'       TIME DIFFERENCE CALCULATION WITH MIDNIGHT CORRECTION
'
          TEMP = TIMER - TIM
          IF TEMP < 0 THEN TEMP = TEMP + 86400
          DIFF = TEMP
'
'
'
        END FUNCTION

        SUB ENABLE
        ON ERROR GOTO TTRAP
        PRINT #1, CHR$(3)

        IF ENAB1$ = "Y" AND ENAB2$ = "Y" THEN
            PRINT #1, "OUT 20,3"
            PRINT #1, "OUT 17,2"
            PRINT #1, "OUT 16,244"
        END IF
        IF ENAB1$ = "Y" AND ENAB2$ = "N" THEN
            PRINT #1, "OUT 20,1"
            PRINT #1, "OUT 17,2"
            PRINT #1, "OUT 16,212"
        END IF
        IF ENAB1$ = "N" AND ENAB2$ = "Y" THEN
            PRINT #1, "OUT 20,2"
            PRINT #1, "OUT 17,2"
            PRINT #1, "OUT 16,180"
        END IF
        IF ENAB1$ = "N" AND ENAB2$ = "N" THEN
            PRINT #1, "OUT 20,0"
            PRINT #1, "OUT 17,2"
            PRINT #1, "OUT 16,148"
        END IF

        END SUB

'
'--------------------------------------------------------------------------------
'SUBROUTINE to create a double line frame on the screen
'--------------------------------------------------------------------------------
'
        SUB FRAME (LEFTCOL%, RIGHTCOL%, TOPROW%, BOTTOMROW%) STATIC
' print the four corners
        LOCATE TOPROW%, LEFTCOL%: PRINT CHR$(201)
        LOCATE TOPROW%, RIGHTCOL%: PRINT CHR$(187)
        LOCATE BOTTOMROW%, LEFTCOL%: PRINT CHR$(200);
        LOCATE BOTTOMROW%, RIGHTCOL%: PRINT CHR$(188);
' print the vertical lines
        FOR VERTLINE% = TOPROW% + 1 TO BOTTOMROW% - 1
          LOCATE VERTLINE%, LEFTCOL%: PRINT CHR$(186);
          LOCATE VERTLINE%, RIGHTCOL%: PRINT CHR$(186);
        NEXT VERTLINE%
' print the horizontal lines
        HORLENGTH% = RIGHTCOL% - LEFTCOL% - 1
        HORLINE$ = STRING$(HORLENGTH%, 205)
        LOCATE TOPROW%, LEFTCOL% + 1: PRINT HORLINE$
        LOCATE BOTTOMROW%, LEFTCOL% + 1: PRINT HORLINE$;
        END SUB

        FUNCTION FSTR$ (DP, NUM AS LONG)


        IF NUM = 0 THEN
           FSTR$ = "N/A"
           GOTO FEXIT
        ELSE
           FOUT = 1 / NUM / TBASE * 1000000 / 2
'           FOUT = FOUT * (1 + (10 ^ -DP) / 2)    'ROUND UP BEFORE TRUNCATING
        END IF
        TFS = STR$(FOUT)
        POSIT = INSTR(TFS, ".")
        FSTR$ = LEFT$(TFS, POSIT + DP)
```

```
FEXIT:  END FUNCTION

        FUNCTION GETRM1$

        MESSG$ = ""
        WHILE LOC(1) <> 0
            A$ = INPUT$(1, #1)
            IF ASC(A$) >= 32 THEN MESSG$ = MESSG$ + A$
            IF DEBUGFLAG% THEN PRINT ASC(A$);
        WEND
        IF DEBUGFLAG% THEN
            PRINT : PRINT "ALPHA MESSAGE RETURNED IS "; MESSG$
            PRINT : DO: LOOP UNTIL INKEY$ = "": INPUT "Press return to continue"; ANS$
        END IF
        GETRM1$ = MESSG$

        END FUNCTION

        FUNCTION GETRM2$

        CALL DELAY(1)
        OSTAT% = TRUE%

        IF LOC(2) = 0 THEN
                OSTAT% = FALSE%
                RSTR$ = "NULL"
                GOTO OMEXIT
        END IF
        MESSG$ = ""
        WHILE LOC(2) <> 0
            A$ = INPUT$(1, #2)
            IF ASC(A$) >= 32 THEN MESSG$ = MESSG$ + A$
            IF DEBUGFLAG% THEN PRINT ASC(A$);
        WEND
        IF DEBUGFLAG% THEN
            PRINT : PRINT "RETURNED OMEGA MESSAGE IS "; MESSG$
            PRINT : DO: LOOP UNTIL INKEY$ = "": INPUT "Press return to continue"; ANS$
        END IF
        IF INSTR(MESSG$, "$") <> 1 THEN
                PRINT "INVALID MESSAGE RETURNED FROM OMEGA"
                OSTAT% = FALSE%
                PRINT CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7)
                GOTO OSTRERR
        ELSEIF INSTR(MESSG$, ":") <> 4 THEN
                PRINT "INVALID MESSAGE RETURNED FROM OMEGA"
                OSTAT% = FALSE%
                PRINT CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7)
                GOTO OSTRERR
        END IF
        DATAEND% = INSTR(5, MESSG$, ":")
        IF DATAEND% = 0 THEN
                PRINT "INVALID MESSAGE RETURNED FROM OMEGA"
                OSTAT% = FALSE%
                PRINT CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7)
                GOTO OSTRERR
        END IF
        AVAL% = HSTRTOI%(MID$(MESSG$, 2, 2))


        IF (AVAL% AND 128) <> 0 THEN
                PRINT "OMEGA TRANSMISSION ERROR"
                PRINT CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7)
                OSTAT% = FALSE%
        END IF
        IF (AVAL% AND 64) <> 0 THEN
                PRINT "OMEGA CHECKSUM ERROR ON INPUT"
                PRINT CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7)
                OSTAT% = FALSE%
        END IF
        IF (AVAL% AND 32) <> 0 THEN
                PRINT "OMEGA SYNTAX ERROR"
                PRINT CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7)
                OSTAT% = FALSE%
        END IF
        IF (AVAL% AND 16) <> 0 THEN
                PRINT "OMEGA COMMUNICATIONS ARE TURNED OFF"
                PRINT CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7)
                OSTAT% = FALSE%
        END IF
        IF (AVAL% AND 8) <> 0 THEN
```

```
                PRINT "OMEGA PARITY ERROR ON INPUT"
                PRINT CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7)
                OSTAT% = FALSE%
        END IF
        IF (AVAL% AND 4) <> 0 THEN
                PRINT "OMEGA THERMO-COUPLE IS OPEN"
                PRINT CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7)
                OSTAT% = FALSE%
        END IF
        IF (AVAL% AND 2) <> 0 THEN
                PRINT "OMEGA IS IN ALARM STATE"
                PRINT CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7)
                END IF
        IF (AVAL% AND 1) <> 0 THEN
                PRINT "UNKNOWN ERROR FROM THE OMEGA"
                PRINT CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7); CHR$(7)
                OSTAT% = FALSE%
        END IF
        IF OSTAT% = FALSE% THEN GOTO OSTRERR

        RSTR$ = MID$(MESSG$, 5, DATAEND% - 5)
        GOTO OMEXIT

OSTRERR:
        RSTR$ = "ERROR"


OMEXIT:
        IF DEBUGFLAG% THEN
                PRINT "OMEGA STATUS WAS  "; AVAL%
                PRINT "OMEGA MESSAGE WAS  "; MESSG$
                PRINT "RETURN VALUE IS   "; RSTR$
                PRINT : DO: LOOP UNTIL INKEY$ = "": INPUT "PRESS RETURN TO CONTINUE"; ANS$
        END IF
        GETRM2$ = RSTR$
        END FUNCTION

        ' FUNCTION TO CONVERT HEX ASCII STRING TO INTEGER
        '
        FUNCTION HSTRTOI% (HSTR$)

        'CONVERT LEFT DIGIT
        HSTRMS$ = MID$(HSTR$, 1, 1)
        HVALMS% = ASC(HSTRMS$) - 48
        IF HVALMS% > 9 THEN HVALMS% = HVALMS% - 7

        'CONVERT RIGHT DIGIT
        HSTRLS$ = MID$(HSTR$, 2, 1)
        HVALLS% = ASC(HSTRLS$) - 48
        IF HVALLS% > 9 THEN HVALLS% = HVALLS% - 7

        'COMBINE AS 1 INTEGER
        HVAL% = HVALLS% + HVALMS% * 16
        HSTRTOI% = HVAL%

        END FUNCTION

        SUB LASERMENU
'
        DIM LMENU$(13)
'
'


        LCHOICE% = 0
        WHILE LCHOICE% <> 13
                LMENUHAD$ = "LASER SETUP OPTIONS"
                LMENU$(1) = "1 Pulse repetition frequency = " + FSTR$(2, PRP) + " Hz"
                LMENU$(2) = "2 Laser 1 duty cycle = " + PSTR$(3, PW1, PRP) + " %"
                LMENU$(3) = "3 Laser 2 duty cycle = " + PSTR$(3, PW2, PRP) + " %"
                LMENU$(4) = "4 Laser 1 Retrigger/cw or Single pulse mode " + RTRIG1$
                LMENU$(5) = "5 Laser 2 Retrigger/cw or Single pulse mode " + RTRIG2$
                LMENU$(6) = "6 Laser 1 enable                             " + ENAB1$
                LMENU$(7) = "7 Laser 2 enable                             " + ENAB2$
                LMENU$(8) = "8 Trigger laser 1"
                LMENU$(9) = "9 Trigger laser 2"
                LMENU$(10) = "A Turn off laser 1"
                LMENU$(11) = "B Turn off laser 2"
                LMENU$(12) = "C Turn off both lasers"
                LMENU$(13) = "R Return to experiment menu"

                CLS
```

```
                    CALL MENU(LMENUNAM$, LMENUS(), LCHOICE%)
                    IF LCHOICE% = 1 THEN
                       PRINT "The current period count is "; PRP; " X "; TBASE * 2; " uS = ";
                       PRINT USING "##.#####"; PRP * 2 * TBASE / 1000000;
                       PRINT " S or "; FSTR$(2, PRP); " Hz "
                       DO: LOOP UNTIL INKEY$ = ""
LC1RP:                 INPUT "What is the desired period count "; PRP
                       PRINT "The updated period count is "; PRP; " X "; TBASE * 2; " uS = ";
                       PRINT USING "##.#####"; PRP * 2 * TBASE / 1000000;
                       PRINT " S or "; FSTR$(2, PRP); " Hz "
                       IF YESNO("Is this setting correct") = FALSE% THEN GOTO LC1RP
                       CALL PULSESET
                    END IF
                    IF LCHOICE% = 2 THEN
                       PRINT "For laser 1:"
                       PRINT "The current period count is "; PRP; " X "; TBASE * 2; " uS = ";
                       PRINT USING "##.#####"; PRP * 2 * TBASE / 1000000;
                       PRINT " S or "; FSTR$(2, PRP); " Hz "
                       PRINT "The current pulse count is "; PW1; " X "; TBASE; " uS = ";
                       PRINT USING "##.#####"; PW1 * TBASE / 1000000;
                       PRINT " S or "; PSTR$(2, PW1, PRP); " % "
                       DO: LOOP UNTIL INKEY$ = ""
LC2RP:                 INPUT "What is the desired pulse count "; PW1
                       PRINT "The current pulse count is "; PW1; " X "; TBASE; " uS = ";
                       PRINT USING "##.#####"; PW1 * TBASE / 1000000;
                       PRINT " S or "; PSTR$(2, PW1, PRP); " % "
                       IF YESNO("Is this setting correct") = FALSE% THEN GOTO LC2RP
                       CALL PULSESET
                    END IF
                    IF LCHOICE% = 3 THEN
                       PRINT "For laser 2:"
                       PRINT "The current period count is "; PRP; " X "; TBASE * 2; " uS = ";
                       PRINT USING "##.#####"; PRP * 2 * TBASE / 1000000;
                       PRINT " S or "; FSTR$(2, PRP); " Hz "
                       PRINT "The current pulse count is "; PW2; " X "; TBASE; " uS = ";
                       PRINT USING "##.#####"; PW2 * TBASE / 1000000;
                       PRINT " S or "; PSTR$(2, PW2, PRP); " % "
                       DO: LOOP UNTIL INKEY$ = ""
LC3RP:                 INPUT "What is the desired pulse count "; PW2
                       PRINT "The current pulse count is "; PW2; " X "; TBASE; " uS = ";
                       PRINT USING "##.#####"; PW2 * TBASE / 1000000;
                       PRINT " S or "; PSTR$(2, PW2, PRP); " % "
                       IF YESNO("Is this setting correct") = FALSE% THEN GOTO LC3RP
                       CALL PULSESET
                    END IF
                    IF LCHOICE% = 4 THEN
                       RTRIG1$ = "S"
                       IF YESNO("DO YOU WANT LASER 1 IN MULTIPLE TRIGGERING/CW MODE OR NOT ") THEN
                          RTRIG1$ = "R"
                       END IF
                    END IF
                    IF LCHOICE% = 5 THEN
                       RTRIG2$ = "S"
                       IF YESNO("DO YOU WANT LASER2 IN MULTIPLE TRIGGERING/CW MODE OR NOT ") THEN
                          RTRIG2$ = "R"
                       END IF
                    END IF
                    IF LCHOICE% = 6 THEN
                       ENAB1$ = "Y"
                       CALL ENABLE
                    END IF
                    IF LCHOICE% = 7 THEN
                       ENAB2$ = "Y"
                       CALL ENABLE
                    END IF
                    IF LCHOICE% = 8 THEN
                       CALL TRIGGER("ONE")
                    END IF
                    IF LCHOICE% = 9 THEN
                       CALL TRIGGER("TWO")
                    END IF
                    IF LCHOICE% = 10 THEN
                       CALL LOFF("ONE")
                       ENAB1$ = "N"
                       CALL ENABLE
                    END IF
                    IF LCHOICE% = 11 THEN
                       CALL LOFF("TWO")
                       ENAB2$ = "N"
                       CALL ENABLE
                    END IF
```

```
                IF LCHOICE% = 12 THEN
                   CALL LOFF("BOTH")
                   ENAB1$ = "N"
                   ENAB2$ = "N"
                   CALL ENABLE
                END IF
        WEND
        END SUB

        SUB LASERON (LASER$)

        IF YESNO("DO YOU WANT TO TURN LASER SYSTEM ON") = FALSE% THEN
                PRINT "SKIPPING TURNING LASERS ON"
                PRINT : PRINT : DO: LOOP UNTIL INKEY$ = "": INPUT "Press return to continue"; ANS$
                GOTO LONEXIT
        END IF
        PRINT "VERIFY THAT LASER SYSTEM IS SAFE FOR ACTIVATION"
        PRINT : PRINT : DO: LOOP UNTIL INKEY$ = "": INPUT "Press return to continue"; ANS$

        IF LASER$ = "ONE" OR LASER$ = "BOTH" THEN
                RT1SAVE$ = RTRIG1$
                RTRIG1$ = "R"
                ENAB1$ = "Y"
                CALL ENABLE
                CALL TRIGGER("ONE")
                RTRIG1$ = RT1SAVE$
        END IF

        IF LASER$ = "TWO" OR LASER$ = "BOTH" THEN
                RT2SAVE$ = RTRIG2$
                RTRIG2$ = "R"
                ENAB2$ = "Y"
                CALL ENABLE
                CALL TRIGGER("TWO")
                RTRIG2$ = RT2SAVE$
        END IF
LONEXIT:
        END SUB

        SUB LOFF (LASER$)
        ON ERROR GOTO TTRAP
        PRINT #1, CHR$(3)
        ANS$ = GETRN1$

        IF LASER$ = "ONE" OR LASER$ = "BOTH" THEN
           PRINT #1, "OUT 17,56"
           IF RTRIG1$ = "R" THEN
                PRINT #1, "OUT 16,53"
           ELSE
                PRINT #1, "OUT 16,49"
           END IF
           PRINT #1, "OUT 17,20"   'CLEAR GATE BIT
           PRINT #1, "OUT 16,0"
        END IF

        IF LASER$ = "TWO" OR LASER$ = "BOTH" THEN
           PRINT #1, "OUT 17,58"
           IF RTRIG2$ = "R" THEN
                PRINT #1, "OUT 16,53"
           ELSE
                PRINT #1, "OUT 16,49"
           END IF
           PRINT #1, "OUT 17,22"   'CLEAR GATE BIT
           PRINT #1, "OUT 16,0"

        END IF


        END SUB

'
'-------------------------------------------------------------------------
' SUBROUTINE to create a menu on the screen
'-------------------------------------------------------------------------
'
'  The MENU subroutine displays a menu on the screen and then elicits
'  a choice from the user. MENU receives a string array of the choices
'  (MENUCHOICES$) and returns an integer (NUMCHOSEN%) indicating the
'  users choice.
'
   SUB MENU (MENUNAME$, MENUCHOICES$(), NUMCHOSEN%) STATIC
```

```
        NUMOFCHOICES% = UBOUND(MENUCHOICES$)
        PROMPT$ = " "
        OKSTRING$ = ""
        LONGSTRING% = 0
        FOR I% = 1 TO NUMOFCHOICES%
          FIRST$ = UCASE$(LEFT$(MENUCHOICES$(I%), 1))
          OKSTRING$ = OKSTRING$ + FIRST$
          PROMPT$ = PROMPT$ + FIRST$ + "  "
          LTEMP% = LEN(MENUCHOICES$(I%))
          IF (LTEMP% > LONGSTRING%) THEN LONGSTRING% = LTEMP%
        NEXT I%
        LONGSTRING% = LONGSTRING% + 1
        PROMPT$ = PROMPT$ + "-> "
        IF (LEN(PROMPT$) >= LONGSTRING%) THEN LONGSTRING% = LEN(PROMPT$) + 1
' test to see if the menu name is longer then the above
        IF (LEN(MENUNAME$) > LONGSTRING%) THEN LONGSTRING% = LEN(MENUNAME$) + 2
        LC% = 37 - (LONGSTRING% \ 2)
        RC% = 80 - LC%
        TC% = 3
        BC% = 10 + NUMOFCHOICES%
        CALL FRAME(LC%, RC%, TC%, BC%)
        FOR I% = 1 TO NUMOFCHOICES%
          LOCATE 6 + I%, LC% + 3
          PRINT UCASE$(LEFT$(MENUCHOICES$(I%), 1)) + ")" + MID$(MENUCHOICES$(I%), 2)
        NEXT I%
        LENNAME% = LEN(MENUNAME$) / 2
        LOCATE 4, 39 - LENNAME%: PRINT MENUNAME$
        LINE$ = STRING$(LONGSTRING%, 196)
        LOCATE 5, LC% + 3: PRINT LINE$
        LOCATE 7 + NUMOFCHOICES%, LC% + 3: PRINT LINE$
        LOCATE 9 + NUMOFCHOICES%, LC% + 3: PRINT PROMPT$;
        CTRLKEYS$ = CHR$(13) + CHR$(27)
        DONE% = FALSE%
        WHILE NOT DONE%
          LOCATE , , 1
          CHARPOS% = 0
          WHILE CHARPOS% = 0
                ANS$ = INKEY$
                IF (ANS$ <> "") THEN
                  ANS$ = UCASE$(ANS$)
                  CHARPOS% = INSTR(OKSTRING$, ANS$)
                  IF (CHARPOS% = 0) THEN BEEP
                END IF
          WEND
          PRINT ANS$
          LOCATE 11 + NUMOFCHOICES%, 23, 0
          PRINT "<Enter> to confirm ; <Esc> to redo";
          NUMCHOSEN% = CHARPOS%
          CHARPOS% = 0
          WHILE CHARPOS% = 0
                ANS$ = INKEY$
                IF (ANS$ <> "") THEN
                  CHARPOS% = INSTR(CTRLKEYS$, ANS$)
                  IF (CHARPOS% = 0) THEN BEEP
                END IF
          WEND
          IF (CHARPOS% = 1) THEN
                DONE% = TRUE%
                CLS
          ELSE
                LOCATE 11 + NUMOFCHOICES%, 23: PRINT SPACE$(35);
                LOCATE 9 + NUMOFCHOICES%, LC% + 3 + LEN(PROMPT$): PRINT " ";
                LOCATE , POS(0) - 1:
          END IF
        WEND
    END SUB

        FUNCTION MVREAD (CHANNEL%)

        ANS$ = GETRN1$
        ANS$ = STR$(CHANNEL% + 47)
        PRINT #1, "OUT 4," + ANS$
        CALL DELAY(1)
        DCOUNT% = 1000
        PRINT #1, "IN 2"
        CALL TWAIT(DCOUNT%)
        LSB$ = GETRN1$
        PRINT #1, "IN 3"
        CALL TWAIT(DCOUNT%)
        MSB$ = GETRN1$
        MVOLTS = (VAL(MSB$) AND 15) * 256 + VAL(LSB$)
```

```
        IF (VAL(MSB$) AND 64) = 0 THEN MVOLTS = -MVOLTS
        IF (VAL(MSB$) AND 32) <> 0 THEN
              PRINT "INPUT VOLTAGE IS OVERRANGE";
              MVOLTS = 9999
        ELSE
              IF DEBUGFLAG% THEN PRINT "THE INPUT VOLTAGE IS "; MVOLTS; "mV";
        END IF
        IF DEBUGFLAG% THEN
              PRINT " LSB of a/d is "; LSB$;
              PRINT " MSB of a/d is "; MSB$;
              PRINT "  PRESS ANY KEY TO EXIT"
        END IF
        ZERO% = 16 ' SELECT ZERO BEFORE EXIT
        ANS$ = STR$(ZERO% + 47)
        PRINT #1, "OUT 4," + ANS$

        MVREAD = MVOLTS

        END FUNCTION

'       Collect the oven data
'
'
        SUB OCOLLECT
        OSETFLAG% = TRUE%
        IF OLENGTH% = 0 OR OINT% = 0 OR OSTEP = 0 THEN OSETFLAG% = FALSE%
        IF OSETFLAG% = FALSE% THEN
              PRINT "OVEN VARIABLES ARE NOT SET PROPERLY"
              GOTO OEXIT
        END IF
        IF ONAMEFLAG% = FALSE% THEN
              IF YESNO("Data will not be saved is this ok") = FALSE% THEN
                    PRINT "EXITING - SET FILENAME IN SETUP MENU."
                    GOTO OEXIT
              END IF
        END IF
        CALL STEPPER(OSTEP, "2")
        PRINT "Q  WILL TERMINATE DATA COLLECTION AT ANY TIME"

        MTIME = TIMER
        DO WHILE DIFF(MTIME) < OLENGTH% * 60! + 1!

              ITIME = INT(DIFF(MTIME))
              FRAC = ITIME / OINT%
              IF INT(FRAC) < FRAC + .01 AND INT(FRAC) > FRAC - .01 THEN

                    PRINT "READING OVEN TEMPERATURE"
                    PRINT #2, "":RPV0:"
                    CALL DELAY(1)
                    MESSG$ = GETRM2$
                    OTEMP = -9999
                    IF MESSG$ <> "ERROR" AND MESSG$ <> "NULL" THEN OTEMP = VAL(MESSG$)

                    IF ONAMEFLAG% THEN
                          PRINT #OFILENO, "TIME IS, "; ITIME; ",S,  OVEN TEMP =, "; OTEMP; ", C"
                    END IF
                    PRINT : PRINT "TIME IS "; ITIME; "S,  OVEN TEMP = "; OTEMP; "; C"
              END IF

              CHAR$ = UCASE$(INKEY$)
              IF CHAR$ = "Q" THEN GOTO OCDONE:

        LOOP


OCDONE: CALL OOFF
        CLOSE #OFILENO
        OFILE$ = ""
        ONAMEFLAG% = FALSE%
OEXIT:
        PRINT : PRINT : DO: LOOP UNTIL INKEY$ = "": INPUT "Press return to continue"; ANS$
        END SUB

        SUB OOFF

        CALL STEPPER(0, "2")

        END SUB

'
'-------------------------------------------------------------------------------
```

```
' SUBROUTINE to open the ALPHA bus
'-------------------------------------------------------------------------
'
'  OPENALPHA is a Subroutine that is used to open the communications
'  to the ALPHA bus. It also resets the controllers and checks
'  for problems.
'
        SUB OPENALPHA STATIC
        ON ERROR GOTO ERTRAP
' open communications to the ALPHA bus.
        OPENCOUNT = 0
TRYAGAIN:
        OPENCOUNT = OPENCOUNT + 1
        IF OPENCOUNT > 2 THEN
           PRINT : PRINT "Check or reset the ALPHA system (turn off, then on)"
           DO: LOOP UNTIL INKEY$ = "": INPUT "PRESS RETURN TO CONTINUE"; ANS$
           OPENCOUNT = 0
        END IF
        CLOSE #1: REM close the file to eliminate possible errors
        PRINT : PRINT "OPENING THE ALPHA BUS FOR COMMUNICATIONS"
        OPEN "COM1:9600,N,8,2,CS,DS,CD" FOR RANDOM AS #1
        CALL DELAY(1)


' initialize the ALPHA bus
        TLOOP = 0
        WHILE TLOOP = 0
          PRINT : PRINT
          PRINT "INITIALIZING THE ALPHA": PRINT
' enter immediate mode with control-c then check for errors
          PRINT #1, CHR$(3)
          CALL DELAY(1)
          PRINT #1, "START"
' check for any problems
          CALL DELAY(1)
          PRINT #1, "ERROR"
          CALL DELAY(2)
          IF LOC(1) = 0 THEN
                PRINT : PRINT "THERE SEEMS TO BE A COMMUNICATIONS PROBLEM"
                PRINT : PRINT "   CHECK THE ALPHA BUS POWER SWITCH"
                PRINT "   CHECK SERIAL PORT CONNECTION"
                PRINT : DO: LOOP UNTIL INKEY$ = "": INPUT "PRESS RETURN TO CONTINUE"; ANS$
                GOTO TRYAGAIN
          ELSE
                TLOOP = 1
          END IF
        WEND
        MESSG$ = GETRN1$
        IF MESSG$ <> "Command was bad" THEN
           PRINT : PRINT "NOT RESET - ABOUT TO TRY AGAIN"
           CALL DELAY(1)
           GOTO TRYAGAIN
        END IF
        PRINT #1, "TERM 0"
        CALL DELAY(1)
        PRINT #1, "TOTAL-RESTART"
        CALL DELAY(3)
        PRINT #1, "ERROR"
        CALL DELAY(1)
        MESSG$ = GETRN1$
        IF DEBUGFLAG% THEN PRINT MESSG$
        IF MESSG$ <> "total-restart " THEN
                PRINT "STEPPER CONTROLLER NOT RESETTING"
                GOTO TRYAGAIN
        END IF
        DWAIT% = 2000
        PRINT #1, CHR$(3)
        CALL TWAIT(DWAIT%)
        PRINT #1, "OUT 17,0"
        CALL TWAIT(DWAIT%)
        PRINT #1, "OUT 16,1"
        CALL TWAIT(DWAIT%)
        ZERO = NVREAD(16)
        IF DEBUGFLAG% THEN
                PRINT "SYSTEM IS RESET"
                PRINT : DO: LOOP UNTIL INKEY$ = "": INPUT "PRESS RETURN TO CONTINUE"; ANS$
                PRINT "ANALOG ZERO IS"; ZERO; "mV."
        END IF
        ON ERROR GOTO 0
        END SUB
```

```
'
'-------------------------------------------------------------------------
' SUBROUTINE to open communications to the OMEGA temp. controller
'-------------------------------------------------------------------------
'
'
        SUB OPENOMEGA STATIC
        ON ERROR GOTO OERTRAP
' open communications to the OMEGA temp. controller.
        OPENCOUNT = 0
OTRYAGAIN:
        OPENCOUNT = OPENCOUNT + 1
        IF OPENCOUNT > 2 THEN
           PRINT : PRINT "Check or reset the OMEGA controller (turn off, then on)"
           DO: LOOP UNTIL INKEY$ = "": INPUT "PRESS RETURN TO CONTINUE"; ANS$
           OPENCOUNT = 0
        END IF
        CLOSE #2 ' Close the file to eliminate possible errors
        PRINT : PRINT "OPENING THE OMEGA CONTROLLER FOR COMMUNICATIONS"
        OPEN "COM2:2400,N,8,2,CS,DS,CD" FOR RANDOM AS #2
        CALL DELAY(1)


' initialize the ALPHA bus
        TLOOP = 0
        WHILE TLOOP = 0
          PRINT : PRINT
          PRINT "INITIALIZING THE OMEGA": PRINT

          PRINT #2, "*:RPV0:"
          CALL DELAY(1)
' check for any problems
          IF LOC(2) = 0 THEN
                PRINT : PRINT "THERE SEEMS TO BE A COMMUNICATIONS PROBLEM"
                PRINT : PRINT "   CHECK THE OMEGA POWER SWITCH"
                PRINT "   CHECK SERIAL PORT CONNECTION"
                PRINT : DO: LOOP UNTIL INKEY$ = "": INPUT "PRESS RETURN TO CONTINUE"; ANS$
                GOTO OTRYAGAIN
          ELSE
                TLOOP = 1
          END IF
        WEND
        MESSG$ = GETRM2$
        IF MESSG$ = "ERROR" OR MESSG$ = "NULL" THEN
           PRINT : PRINT "NOT RESET - ABOUT TO TRY AGAIN"
           CALL DELAY(1)
           GOTO OTRYAGAIN
        END IF
        ANS$ = GETRM2$
        IF DEBUGFLAG% THEN
                PRINT "THE SYSTEM TEMPERATURE IS "; VAL(MESSG$)
                PRINT "FINAL READ GAVE "; ANS$
                PRINT : PRINT "SYSTEM IS RESET"
                PRINT : DO: LOOP UNTIL INKEY$ = "": INPUT "PRESS RETURN TO CONTINUE"; ANS$
        END IF
        ON ERROR GOTO 0
        END SUB

        SUB OTERM
        PRINT "ENTERING OMEGA TERMINAL MODE (esc) KEY QUITS."
        ON ERROR GOTO TTRAP
        A$ = ""
        QUIT$$ = CHR$(27)
        DO

          A$ = INKEY$
          IF A$ = QUIT$$ THEN
                EXIT DO
          ELSEIF A$ <> "" THEN
                PRINT #2, A$;
                PRINT A$;
          END IF
          IF LOC(2) THEN
                PRINT INPUT$(LOC(2), #2);
          END IF
        LOOP
        ANS$ = GETRM2$

        END SUB

        SUB OVENSET
```

```
        DIM OMENUS(5)
'
'

        OCHOICE% = 0
        WHILE OCHOICE% <> 5
                OMENUNAM$ = "OVEN SETUP OPTIONS"
                OMENUS(1) = "1 Oven data filename or none " + OFILE$
                OMENUS(2) = "2 Oven test duration " + STR$(OLENGTH%) + " min."
                OMENUS(3) = "3 Data collection interval " + STR$(OINT%) + " s."
                OMENUS(4) = "4 Stepper speed (cw is +) " + STR$(OSTEP) + " /s or " + STR$(RPM(OSTEP)) + " RPM."
                OMENUS(5) = "r Return to experiment menu"
                CLS
                CALL MENU(OMENUNAM$, OMENUS(), OCHOICE%)
                IF OCHOICE% = 1 THEN
                        IF YESNO("Do you want to save the data on disk") THEN
                                CALL DATAFILENAME(OFILE$, OFILENO)
                                ONAMEFLAG% = TRUE%
                        ELSE
                                OFILE$ = ""
                                ONAMEFLAG% = FALSE%
                        END IF
                END IF
                IF OCHOICE% = 2 THEN
                        INPUT "Enter the total experiment duration in minutes"; OLENGTH%
                END IF
                IF OCHOICE% = 3 THEN
ODOIN:                  INPUT "Enter the data collection interval in seconds"; OINT%
                        IF OINT% < 10 THEN
                                PRINT "Interval must be 10s or more - try again"
                                GOTO ODOIN
                        END IF
                END IF
                IF OCHOICE% = 4 THEN
                        PRINT "The current step rate is "; OSTEP; "steps/s  or ";
                        PRINT RPM(OSTEP); " RPM"
                        DO: LOOP UNTIL INKEY$ = ""
OSTEPRD:                INPUT "Enter the desired stepper rate in steps /s cw is - ccw is + "; OSTEP
                        PRINT "The updated step rate is "; OSTEP; "steps/s  or ";
                        PRINT RPM(OSTEP); " RPM"
                        IF YESNO("Is this setting correct") = FALSE% THEN GOTO OSTEPRD
                END IF
        WEND


        END SUB

'       PRINT TRUNCATION PROGRAMME FOR FLOAT STRINGS
'
'
        FUNCTION PSTR$ (DP, NUM AS LONG, PWB2 AS LONG)

        IF NUM = 0 OR PWB2 = 0 THEN
           PSTR$ = "N/A"
           GOTO PEXIT
        ELSE
           POUT = NUM / PWB2 / 2 * 100
'           POUT = POUT * (1 + (10 ^ -DP) / 2)     'ROUND UP BEFORE TRUNCATING
        END IF
        PSTR$ = STR$(POUT)
        POSIT = INSTR(PS, ".")
'       THE FOLLOWING NEEDS FIXING TO PREVENT ERRORS IN EXPONENT DISPLAYS
'        PSTR$ = LEFT$(PS, POSIT + DP)
'        PRINT : DO: LOOP UNTIL INKEY$ = "": INPUT "PRESS RETURN TO CONTINUE"; ANS$

PEXIT:  END FUNCTION

        SUB PULSESET
        ON ERROR GOTO TTRAP
        PRINT #1, CHR$(3)
        DIM MSB AS LONG, LSB AS LONG
        MSB = INT(PRP / 256)
        LSB = PRP - MSB * 256
        IF DEBUGFLAG% THEN
                PRINT "MASTER COUNT MSB IS "; MSB; "LSB IS "; LSB
                INPUT "PRESS RETURN TO CONTINUE"; ANS$
        END IF
        PRINT #1, "OUT 17,52"
        PRINT #1, "OUT 16," + STR$(MSB)
        PRINT #1, "OUT 17,54"
        PRINT #1, "OUT 16," + STR$(LSB)
```

```
        MSB = INT(PW1 / 256)
        LSB = PW1 - MSB * 256
        IF DEBUGFLAG% THEN
                PRINT "COUNTER 1 MSB IS "; MSB; "LSB IS "; LSB
                INPUT "PRESS RETURN TO CONTINUE"; ANS$
        END IF
        PRINT #1, "OUT 17,44"
        PRINT #1, "OUT 16," + STR$(MSB)
        PRINT #1, "OUT 17,46"
        PRINT #1, "OUT 16," + STR$(LSB)

        MSB = INT(PW2 / 256)
        LSB = PW2 - MSB * 256
        IF DEBUGFLAG% THEN
                PRINT "COUNTER 2 MSB IS "; MSB; "LSB IS "; LSB
                INPUT "PRESS RETURN TO CONTINUE"; ANS$
        END IF
        PRINT #1, "OUT 17,48"
        PRINT #1, "OUT 16," + STR$(MSB)
        PRINT #1, "OUT 17,50"
        PRINT #1, "OUT 16," + STR$(LSB)

        PRINT #1, "OUT 17,60"       'ENABLE AND START THE MASTER DIVIDER
        PRINT #1, "OUT 16,226"
        PRINT #1, "OUT 17,24"
        PRINT #1, "OUT 16,6"
        END SUB

'       Collect the reactor data
;
;
        SUB RCOLLECT
        RSETFLAG% = TRUE%
        IF PRP = 0 OR PW1 = 0 OR PW2 = 0 THEN
                PRINT "LASER PARAMETERS ARE NOT SET - EXITING"
                RSETFALG% = FALSE%
                GOTO REXIT
        END IF
        IF RLENGTH% = 0 OR RINT% = 0 OR RSTEP = 0 THEN RSETFLAG% = FALSE%
        IF RSETFLAG% = FALSE% THEN
                PRINT "REACTOR VARIABLES ARE NOT SET PROPERLY"
                GOTO REXIT
        END IF
        IF RNAMEFLAG% = FALSE% THEN
                IF YESNO("Data will not be saved is this ok") = FALSE% THEN
                        PRINT "EXITING - SET FILENAME IN SETUP MENU."
                        GOTO REXIT
                END IF
        END IF
        CALL STEPPER(-RSTEP, "1")
        CALL LASERON("BOTH")
        PRINT "Q  WILL TERMINATE DATA COLLECTION AT ANY TIME"

        MTIME = TIMER
        DO WHILE DIFF(MTIME) < RLENGTH% * 60! + 1!

                ITIME = INT(DIFF(MTIME))
                FRAC = ITIME / RINT%
                IF INT(FRAC) < FRAC + .01 AND INT(FRAC) > FRAC - .01 THEN

                        PRINT "READING ANALOG VALUES"
                        LASER1P = HVREAD(1) / 10
                        LASER2P = HVREAD(2) / 10
                        RTEMP = HVREAD(3)
                        IF RNAMEFLAG% THEN
                                PRINT #RFILENO, "TIME IS, "; ITIME; ",S LASER1 =, "; LASER1P;
                                PRINT #RFILENO, ",LASER2 =, "; LASER2P; ",REACTOR TEMP =, "; RTEMP; ", C"
                        END IF
                        PRINT : PRINT "TIME IS "; ITIME; "S LASER1 = "; LASER1P; "LASER2 = "; LASER2P;
                        PRINT "REACTOR TEMP = "; RTEMP; " C"
                END IF

                CHAR$ = UCASE$(INKEY$)
                IF CHAR$ = "Q" THEN GOTO RCDONE:

        LOOP


RCDONE: CALL ROFF
        CLOSE #RFILENO
```

```
        RFILE$ = ""
        RNAMEFLAG% = FALSE%
REXIT:
        PRINT : PRINT : DO: LOOP UNTIL INKEY$ = "": INPUT "Press return to continue"; ANS$
        END SUB

' .
SUB REACTORSET
        DIM RMENU$(5)
'
'

        RCHOICE% = 0
        WHILE RCHOICE% <> 5
                RMENUNAM$ = "REACTOR SETUP OPTIONS"
                RMENU$(1) = "1 Reactor data filename or none " + RFILE$
                RMENU$(2) = "2 Reactor test duration " + STR$(RLENGTH%) + " min."
                RMENU$(3) = "3 Data collection interval " + STR$(RINT%) + " s."
                RMENU$(4) = "4 Stepper speed (cw is +) " + STR$(RSTEP) + " /s or " + STR$(RPM(RSTEP)) + " RPM."
                RMENU$(5) = "r Return to experiment menu"
                CLS
                CALL MENU(RMENUNAM$, RMENU$(), RCHOICE%)
                IF RCHOICE% = 1 THEN
                        IF YESNO("Do you want to save the data on disk") THEN
                                CALL DATAFILENAME(RFILE$, RFILENO)
                                RNAMEFLAG% = TRUE%
                        ELSE
                                RFILE$ = ""
                                RNAMEFLAG% = FALSE%
                        END IF
                END IF
                IF RCHOICE% = 2 THEN
                        INPUT "Enter the total experiment duration in minutes"; RLENGTH%
                END IF
                IF RCHOICE% = 3 THEN
RDOIN:                  INPUT "Enter the data collection interval in seconds"; RINT%
                        IF RINT% < 10 THEN
                                PRINT "Interval must be 10s or more - try again"
                                GOTO RDOIN
                        END IF
                END IF
                IF RCHOICE% = 4 THEN
                        PRINT "The current step rate is "; RSTEP; "steps/s  or ";
                        PRINT RPM(RSTEP); " RPM"
                        DO: LOOP UNTIL INKEY$ = ""
RSTEPRD:                INPUT "Enter the desired stepper rate in steps /s cw is - ccw is + "; RSTEP
                        PRINT "The updated step rate is "; RSTEP; "steps/s  or ";
                        PRINT RPM(RSTEP); " RPM"
                        IF YESNO("Is this setting correct") = FALSE% THEN GOTO RSTEPRD
                END IF
        WEND

END SUB

        SUB ROFF

        CALL LOFF("BOTH")
        ENAB1$ = "N"
        ENAB2$ = "N"
        CALL ENABLE
        CALL STEPPER(0, "1")

        END SUB

        FUNCTION RPM (STEPS)

        RPM = STEPS / 200 / 72 * 15 * 60

        END FUNCTION

'
'-------------------------------------------------------------------------------
' SUBROUTINE FOR SPECIAL CONFIGURATIONS
'-------------------------------------------------------------------------------
'
        SUB SPECIALCONFIG STATIC
        CLS : PRINT
        PRINT "THIS SUBROUTINE IS USED FOR SPECIAL CONFIGURATIONS"
        PRINT "**************************************************"
        PRINT : PRINT
        PRINT "    This subroutine must be written and setup by the"
```

```
        PRINT "    user. It can be very useful since it can make use"
        PRINT "    of all of the subroutines that are included in the"
        PRINT "    program called LASER.BAS."
        PRINT
        PRINT
        PRINT : DO: LOOP UNTIL INKEY$ = "": INPUT "PRESS RETURN TO CONTINUE"; ANS$
        END SUB

        SUB STEPPER (SPEED, MOTOR$)

        DWAIT% = 3000
        PRINT #1, "TERM 0"
        CALL TWAIT(DWAIT%)

        IF SPEED = 0 THEN
                PRINT #1, "S M"; MOTOR$
                CALL TWAIT(DWAIT%)
        ELSE
                PRINT #1, "HF M"; MOTOR$; " 0"
                CALL TWAIT(DWAIT%)
                PRINT #1, "DT M"; MOTOR$; " FULL"
                CALL TWAIT(DWAIT%)
                IF SPEED < 0 THEN
                        PRINT #1, "DT M"; MOTOR$; " HALF"
                        CALL TWAIT(DWAIT%)
                        PRINT #1, "SP M"; MOTOR$; " "; -SPEED
                        CALL TWAIT(DWAIT%)
                        PRINT #1, "GO M"; MOTOR$; " ND"
                        CALL TWAIT(DWAIT%)
                ELSE
                        PRINT #1, "DT M"; MOTOR$; " HALF"
                        CALL TWAIT(DWAIT%)
                        PRINT #1, "SP M"; MOTOR$; " "; SPEED
                        CALL TWAIT(DWAIT%)
                        PRINT #1, "GO M"; MOTOR$; ""
                        CALL TWAIT(DWAIT%)
                END IF
        END IF
        PRINT #1, CHR$(3)
        CALL TWAIT(DWAIT%)

        END SUB

        SUB TIMERINIT

' ENSURE WE ARE NOT IN TERMINAL MODE
        ON ERROR GOTO TTRAP
        PRINT #1, CHR$(3)
        ANS$ = GETRM1$

' RESET AND SETUP MODES AND PORTS
        PRINT #1, "OUT 17,0"
        PRINT #1, "OUT 16,1"      ' RESET
        PRINT #1, "OUT 16,0"

        PRINT #1, "OUT 17,2"
        PRINT #1, "OUT 16,148"    ' MASTER CONTROL

        PRINT #1, "OUT 17,12"
        PRINT #1, "OUT 16,14"     ' PORT C DIRECTION

        PRINT #1, "OUT 17,86"
        PRINT #1, "OUT 16,238"    ' PORT B DIRECTION

' SET TO 64 uS TIME BASE
        PRINT #1, "OUT 17,26"
        PRINT #1, "OUT 16,6"
        TBASE = 64

' SET ALL THE DIVIDE REGESTERS
        CALL PULSESET

        ENAB1$ = "N"
        ENAB2$ = "N"
        CALL ENABLE
' TURN INTERLOCKS OFF
        PRINT #1, "OUT 23,130"
        PRINT #1, "OUT 20,0"
        END SUB

        SUB TRIGGER (LASER$)
```

```
        ON ERROR GOTO TTRAP
        PRINT #1, CHR$(3)
        ANS$ = GETRN1$

        IF LASER$ = "ONE" OR LASER$ = "BOTH" THEN
           PRINT #1, "OUT 17,56"
           IF RTRIG1$ = "R" THEN
                PRINT #1, "OUT 16,117"
           ELSE
                PRINT #1, "OUT 16,101"
           END IF
           PRINT #1, "OUT 17,20"   'SET GATE AND TRIGGER BITS
           PRINT #1, "OUT 16,6"
        END IF

        IF LASER$ = "TWO" OR LASER$ = "BOTH" THEN
           PRINT #1, "OUT 17,58"
           IF RTRIG2$ = "R" THEN
                PRINT #1, "OUT 16,117"
           ELSE
                PRINT #1, "OUT 16,101"
           END IF
           PRINT #1, "OUT 17,22"   'SET GATE AND TRIGGER BITS
           PRINT #1, "OUT 16,6"

        END IF

        END SUB

        SUB TWAIT (COUNTS%)
        COUNT% = COUNTS%
        DO WHILE COUNT% > 0
        COUNT% = COUNT% - 1
        LOOP
        END SUB

'
'-------------------------------------------------------------------------------
' FUNCTION to test for keyboard decision making
'-------------------------------------------------------------------------------
'
        FUNCTION YESNO (PROMPT$)

'YESNO.BAS
' The YESNO function asks the user a question and returns a Boolean
' value indicating the response: true(-1) for yes, false(0) for no
'
        DO: LOOP UNTIL INKEY$ = ""
        PRINT PROMPT$; " (Y OR N) ->";
        REPLY$ = ""
        CHECK = FALSE%
        WHILE CHECK = FALSE%
          INPUT REPLY$
          REPLY$ = UCASE$(REPLY$)
          IF (REPLY$ <> "") THEN
                IF (REPLY$ <> "Y" AND REPLY$ <> "N") THEN
                    BEEP
                    DO: LOOP UNTIL INKEY$ = ""
                    PRINT PROMPT$; " (Y OR N) ->";
                ELSE
                    CHECK = TRUE%
                END IF
          END IF
        WEND
        YESNO = (REPLY$ = "Y")

        END FUNCTION
```

Appendix C

A copy of the issued U.S. patent

United States Patent [19]

Wilson et al.

[11] **Patent Number: 5,037,785**

[45] **Date of Patent: Aug. 6, 1991**

[54] **CATALYST REGENERATION PROCESS USING LASER RADIATION**

[75] Inventors: **Michael F. Wilson, Ottawa; Thomas M. Steel, Downsview; Walter W. Duley, King City, all of Canada**

[73] Assignee: **Her Majesty in the Queen Right of Canada as represented by the Minister of Energy, Mines and Resources, Ottawa, Canada**

[21] Appl. No.: **438,634**

[22] Filed: **Nov. 17, 1989**

[51] Int. Cl.[5] **B01J 37/34**; B01J 38/14; C10G 45/08

[52] U.S. Cl. ..... **502/5**; 204/157.41; 208/108; 208/111; 208/140; 208/144; 208/216 R; 208/254 H; 502/38; 502/522

[58] Field of Search 502/5, 38–43, 502/522; 204/157.41, 157.51, 157.61

[56] **References Cited**

U.S. PATENT DOCUMENTS

2,758,098	8/1956	Haensel	502/34
4,012,301	3/1977	Rich et al.	204/157.41
4,124,466	11/1978	Morrey	204/157.41
4,144,189	3/1979	Kirkbridge	252/414
4,551,437	11/1985	Berrebi	502/522
4,849,199	7/1989	Pinneo	423/446
4,970,397	11/1990	Green et al.	502/522

FOREIGN PATENT DOCUMENTS

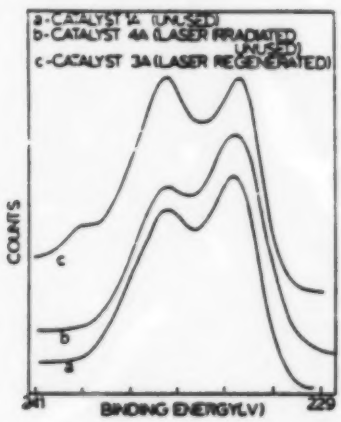
0128302	12/1984	European Pat. Off.	
0202911	11/1986	European Pat. Off.	
1105224	7/1984	U.S.S.R.	502/38

Primary Examiner—Paul E. Konopka
Attorney, Agent, or Firm—Darby & Darby

[57] **ABSTRACT**

A process for regeneration of a deactivated hydroprocessing catalyst is provided. The process comprises exposing the catalyst to laser radiation in the presence of an oxidizing gas. The process may be used to regenerate supported or unsupported metal catalysts which have been fouled by coking.

23 Claims, 4 Drawing Sheets



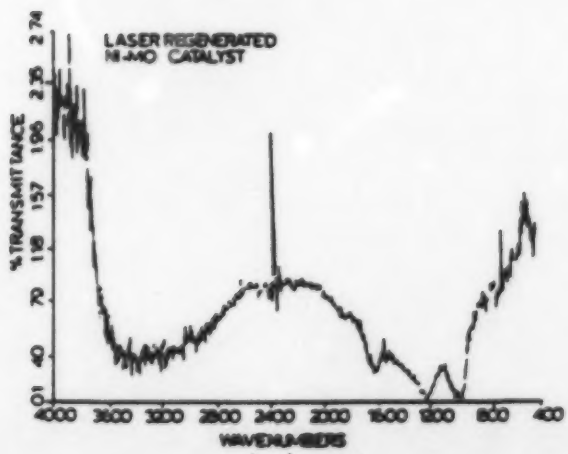
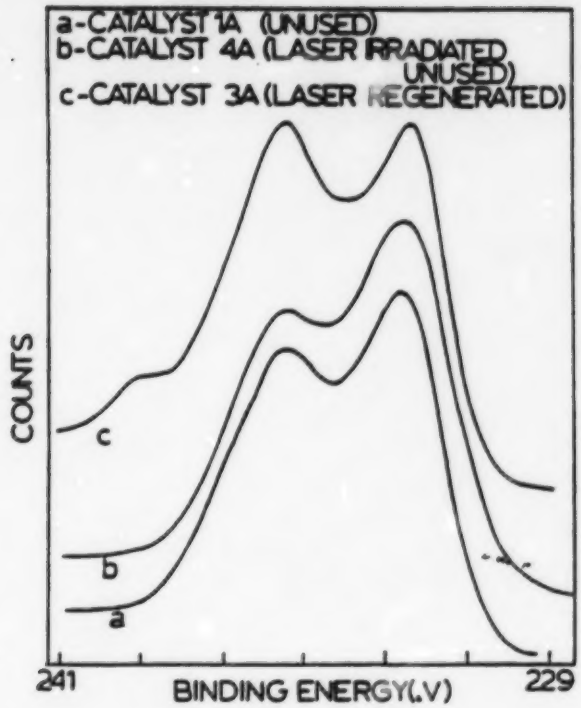


FIG. 5


a-CATALYST 1A (UNUSED)
b-CATALYST 4A (LASER IRRADIATED UNUSED)
c-CATALYST 3A (LASER REGENERATED)
COUNTS
c
b
a
241
BINDING ENERGY(.V)
229

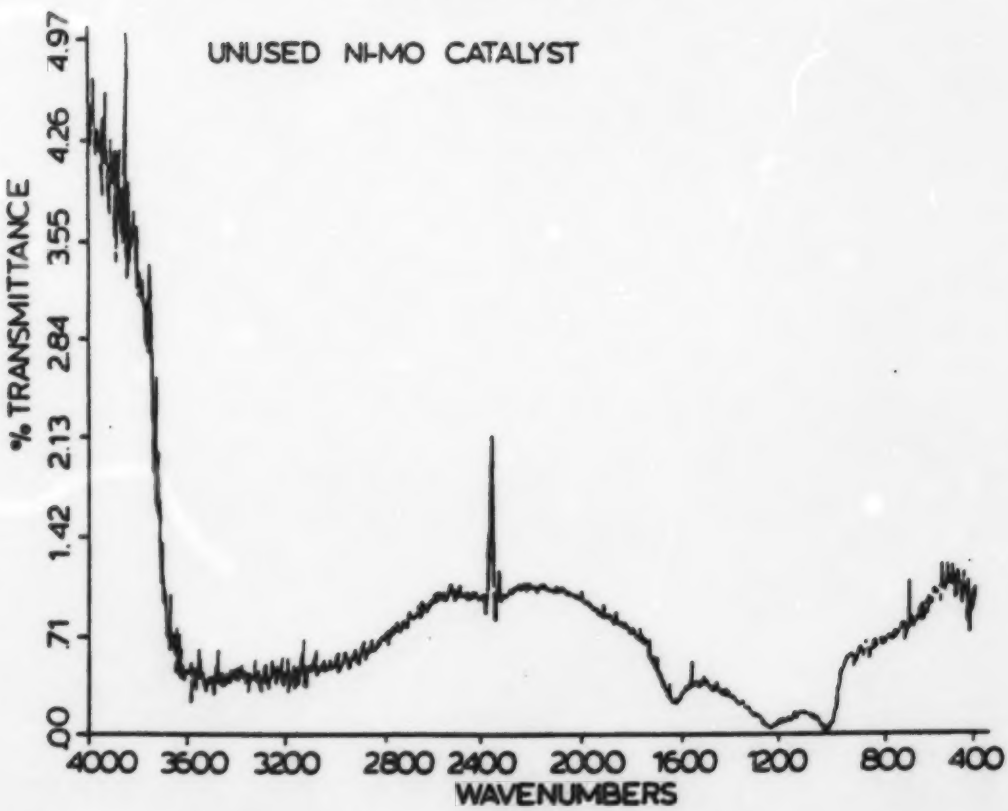
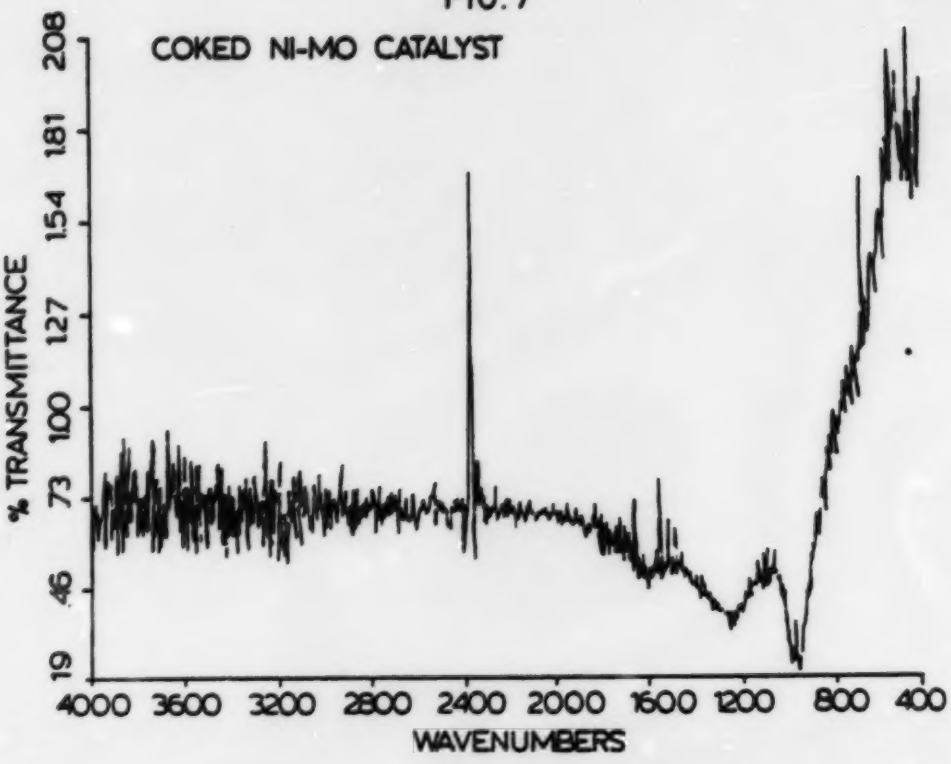

UNUSED NI-MO CATALYST
% TRANSMITTANCE
4.97
4.26
3.55
2.84
2.13
1.42
.71
.00
4000
3500
3200
2800
2400
2000
1600
1200
800
400
WAVENUMBERS

FIG. 6

FIG. 7


COKED NI-MO CATALYST
% TRANSMITTANCE
208
181
154
127
100
73
46
19
4000 3600 3200 2800 2400 2000 1600 1200 800 400
WAVENUMBERS

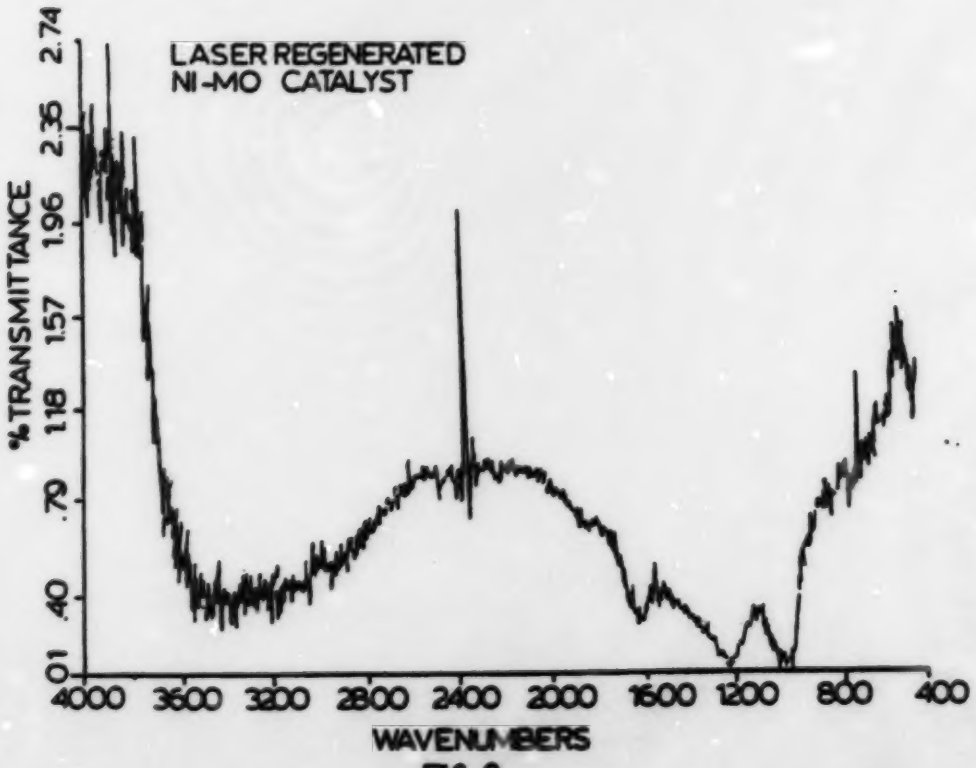

LASER REGENERATED
NI-MO CATALYST
% TRANSMITTANCE
2.74
2.35
1.96
1.57
1.18
.79
.40
01
4000 3600 3200 2800 2400 2000 1600 1200 800 400
WAVENUMBERS

FIG. 8

CATALYST REGENERATION PROCESS USING LASER RADIATION

FIELD OF THE INVENTION

The present invention relates to a process for regenerating a deactivated hydroprocessing catalyst.

BACKGROUND OF THE INVENTION

The use of hydroprocessing catalysts in the petroleum industry is known and is well documented. Generally, hydroprocessing catalysts encompass both hydrotreating and hydrocracking catalysts. Typically, hydrotreating catalysts are utilized to facilitate removal of organosulphur and nitrogen compounds from refinery feedstocks as a treatment step prior to quality assessment of the final fuel product. Similarly, hydrocracking catalysts may be used in processes for converting gas oils to transportation fuels and for refining lube oils. The cost associated with these catalysts (i.e. the cost of obtaining/purchasing and of using the catalysts) represents the major cost associated with the conversion of primary hydrocarbons to refined fuel products.

Hydroprocessing catalysts generally comprise molybdate and/or tungstate catalysts promoted by nickel and/or cobalt and supported on an inert material, usually gamma alumina. Typically, commercial hydroprocessing catalysts are prepared by supporting the active metal oxides (e.g. MoO_3, WO_3) on γ-Al_2O_3. This supporting process may involve successive impregnation/-calcination steps followed by promotion with CoO or NiO. After loading into a reactor, the catalysts are activated for hydroprocessing operations by a sulphidation step which serves to convert the supported metal oxide-based catalyst to the more stable metal suphide-based (e.g. MoS_2, WS_2) catalyst. During hydroprocessing, the catalyst activity is usually sustained by the presence of organosulphur compounds in the feedstocks. These compounds supply sulphur to the catalyst through hydrogen sulphide (H_2S) formation.

As the price of crude oil has declined in recent years, petroleum refiners in general and synthetic crude oil producers in particular have been devoting considerable effort toward developing techniques by which process efficiency will be increased and/or overall process costs will be decreased.

Consideration has been given to developing processes for regenerating deactivated or spent hydrotreating catalysts. Bogdanor et al (*Ind. Eng. Chem. Prod. Res. Dev.* 1986, 25, 220–230) teach that deactivation of hydrotreating process occurs in at least four different ways:

(i) fouling by depositing of coke, ash and metals;
(ii) sintering of the support with consequent loss of surface area;
(iii) agglomeration of active metals; and
(iv) poisoning of active sites on catalysts (usually by metals contained in feedstock).

Of these, it is believed that fouling is the major cause of deterioration in catalyst performance. Fouling involves the deposition of carbonaceous matter on the catalyst surface (usually referred to as coke). This has at least two deleterious results: (a) physical blockage of the catalytically active surface sites and, on a larger scale, (b) plugging of catalyst pores such that diffusion of the feedstock through the pores to the active sites is impeded. Coke fouling of catalytic sites usually occurs via adsorption of certain molecular species (referred to as coking precursors) which are bound strongly to the sites and may be easily polymerized and/or condensed to form large molecular structures.

Excessive operating temperatures may cause sintering and/or agglomeration of hydrotreating catalysts through crystal growth. Sintering is an irreversible phenomenon whereas redispersion of agglomerated metals is practised industrially.

Catalyst poisoning by metals usually involves contamination of the active sites by, for example, lead, arsenic and sodium contained in the feedstock being treated. Catalyst poisoning differs from fouling in that the former represents a chemical interaction of the feedstock material with the catalyst surface, whereas the latter is a physical phenomenon.

Some of the largest producers of synthetic crude oil may be found in Alberta, Canada. Since hydroprocessing operations in synthetic fuels production involves exposing the catalyst to more severe operating regimes than those used in conventional crude oil refining processes, the hydroprocessing catalysts used by synthetic fuel producers may be considered as a higher risk investment. Upgraded bitumen from fluid and delayed coking operations usually requires hydrotreating prior to blending of distillate streams and pipelining as synthetic crude oil. In such a case, the hydrotreating processes may be used to remove sulphur and nitrogen heteroatoms, and to saturate olefins and some aromatics in naphtha and gas oil coker distillates. Alternatively, the catalysts may be used in refinery hydrocracking operations for upgrading synthetic crude gas oils and lube oils. In such a case, more severe reactions conditions are required with the result that the catalysts may experience considerable fouling (i.e. coking) during the operating cycle.

As used throughout this specification, the term "hydroprocessing catalyst" is meant to encompass catalyst which are deactivated by coke fouling. Nonlimiting examples of such catalysts are those used for hydrotreating hydrodesulphurization, hydrodenitrogenation, and hydrogenation of olefins and aromatics), hydrocracking, gasoline reforming, selective hydrogenation of pyrolysis gasolines, and those used as molecular sieves.

Generally, efficient and successful operation of a commercial hydroprocessing unit involves maintenance of maximum feedstock conversion levels throughout the lifetime of the active catalyst. As the catalyst slowly deactivates, the process temperature is systematically ramped upwardly until the catalyst activity is substantially exhausted—i.e. the catalyst is deactivated or spent. If the appropriate precautionary steps are taken, the catalyst will be reversibly deactivated—i.e. it will be fouled. In this type of operating cycle, catalyst lifetime will typically vary from six to eighteen months depending on feedstock composition and operating conditions. Generally, hydroprocessing light petroleum fractions permits a longer catalyst lifetime when compared to hydroprocessing heavy gas oils. The frequency of reactor downtime is related to the activity and/or the lifetime of the catalyst and to the composition of the feedstock material.

BRIEF DESCRIPTION OF THE PRIOR ART

Fouled hydroprocessing catalysts may be regenerated by burning off surface carbon via an oxidative regeneration process. Typically, such a regeneration

process involves reaction of the deactivated catalyst in the presence of an oxidizing air stream (usually air or air diluted with nitrogen) in a high temperature furnace.

Furimsky (*Applied Catalysis*, 44 (1988) 189-198) teaches that catalysts used to hydrotreat light or medium distillate fractions may be regenerated to a greater extent than catalysts used to treat heavy residues. Moreover, this reference teaches that, in a conventional catalyst regeneration process (i.e. high temperature burn-off), the initial contact between the coke molecules on the catalyst surface and the oxidizing medium may result in uncontrollable overheating and possibly sintering of the catalyst. This should be avoided as it can result in permanent and undesirable changes to the catalyst rendering it unusable.

Yoshimura and Furimsky (*Applied Catalysis*, 23 (1986) 157-171) teach that, in conventional oxidative catalyst regeneration processes, temperatures as high as 500° C. may be required to burn off the carbonaceous material from the catalyst surface. The potential problems associated with exposing hydrotreating catalysts to high temperatures is discussed above.

U.S. Pat. No. 2,758,098 (to Universal Oil Products Company) teaches a process for regeneration of platinum-containing catalysts which have been rendered relatively inactive as a result of use in a hydrocarbon conversion process. Generally, the process encompasses periodically contacting the spent catalysts with carbon dioxide at temperatures of from 1100° to 1400° F. (i.e. from 594° to 760° C.) for a period of time sufficient to render the catalyst active. It is interesting to note that the residence time required to regenerate the catalyst utilizing the subject process is on the order of one hour or more. Essentially, this reference teaches a conventional high temperature, long residence time, oxidative catalyst regeneration process. Notwithstanding the required residence time (which decreases efficiency of regeneration process , the disadvantage of exposing catalysts to high temperatures is discussed above.

It should be appreciated that conventional high temperature oxidative catalyst regeneration processes generally do not result in restoration of the catalyst to the original level of activity. After each time the catalyst is regenerated, the restored catalyst can usually only be used for a shorter period of time before requiring further regeneration. It is likely that this is due to an unavoidable degree of sintering of the catalyst which is associated with many conventional high temperature oxidative regeneration processes. Thus, using such a process to regenerate the catalyst results in a definite limit of catalyst lifetime.

It is an object of the present invention to provide a process for the regeneration of deactivated hydroprocessing catalysts which obviates or mitigates the above-mentioned disadvantages of the prior art.

It is another object of the present invention to provide a hydroprocessing catalyst regeneration process during which the occurrence of catalyst overheating is minimized or substantially eliminated.

SUMMARY OF THE INVENTION

Accordingly, the present invention provides a process for regenerating a deactivated hydroprocessing catalyst which comprises exposing said catalyst to laser radiation in the presence of an oxidizing gas. The type of laser radiation utilized in the process is not particularly restricted.

The hydroprocessing catalyst suitable for use in the present process is one which has been substantially deactivated by fouling. Thus, in accordance with the present process, carbonaceous material (e.g. coke) is removed from the catalyst surface via photo-thermally induced chemical reaction of the material with the oxidizing gas.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the present invention will be described with reference to the accompanying drawings, in which:

FIG. 1 is a scanning electron micrograph of an unused hydroprocessing catalyst;

FIG. 2 is a scanning electron micrograph of a fouled hydroprocessing catalyst;

FIG. 3 is a scanning electron micrograph of a hydroprocessing catalyst which has been regenerated according to the present process;

FIG. 4 is a scanning electron micrograph of an unused, laser irradiated hydroprocessing catalyst;

FIG. 5 is an X-ray photoelectron spectrum of three hydroprocessing catalysts;

FIG. 6 is an infrared spectrum of an unused hydroprocessing catalyst;

FIG. 7 is an infrared spectrum of a fouled hydroprocessing catalyst; and

FIG. 8 is an infrared spectrum of a hydroprocessing catalyst which has been regenerated according to the present process.

DETAILED DESCRIPTION OF THE INVENTION

The process of the present invention provides an improved method of hydroprocessing catalyst regeneration which may be used to avoid at least some of the disadvantages associated with the prior art processes discussed above. Thus, the present invention contemplates exposing a deactivated catalyst to radiation from a laser in the presence of an oxidizing gas.

The deactivated hydroprocessing catalyst is typically in the form of particles and may comprise extrudates, spheres, trilobes or quadrilobes. Preferably, the deactivated hydroprocessing catalyst is regenerated in a reactor which is adapted to allow for agitation or movement of the particles such that complete and even surface exposure to the laser radiation is facilitated. The residence time during which the catalyst is exposed to the laser radiation depends, in part, on the size of the catalyst particles and the vigour with which they are agitated. For example, use of a batch of small catalyst particles (i.e 20-50 mesh) in conjunction with agitation will necessitate a relatively short exposure time, typically on the order of from about 1 to about 3 seconds. Given the particle size, the required exposure time can be readily determined by a person skilled in the art.

Alternatively, the catalyst may be of the type which is deposited on or adhered as a coating to the surface of a substrate. For example, the catalyst may form a thin coating (e.g. from 10 to 100 μm) on a flat metal substrate. In such a case, the catalyst may be regenerated very efficiently (i.e. relatively short exposure time to laser radiation) since agitation would not be required.

Although not wishing to be bound by any particular theory or mode of operation, the Applicants believe that carbonaceous matter (e.g. coke) is removed from the surface of the catalyst via photo-thermally induced

chemical reaction between the matter and the oxidizing gas.

The term "oxidizing gas" as used in this specification is intended to include a pure oxidizing gas and composite gas mixtures comprising an oxidizing gas. A non-limiting example of a suitable oxidizing gas is oxygen. In most applications, the use of pure oxygen is relatively hazardous due to its highly inflammable nature. Thus, it is preferred to use an oxidizing gas comprising from about 15 to about 25 weight percent of oxygen. A particularly preferred embodiment of the present process encompasses the use of air (typically comprising from about 20 to about 21 weight percent of oxygen) as the oxidizing gas. It should be appreciated that the temperature of the reaction between the oxidizing gas and the carbonaceous matter may be controlled to a certain degree by controlling the inflow of oxidizing gas. Such control, which can be instituted as an in-process refinement, is within the capabilities of a person skilled in the art.

As stated above, the hydroprocessing catalyst suitable for use in the process of the present invention is one which has been substantially deactivated by fouling. The type of hydroprocessing catalyst suitable for use in the process of the present invention is not particularly restricted. Many hydroprocessing catalysts are available commercially. The preferred catalysts include supported metals or metal sulphides, on a suitable support material. Suitable metal sulphides include molybdenum and tungsten sulphides, preferably promoted by sulphides of cobalt or nickel. Non-limiting examples of suitable metals include iron, chromium, cobalt, nickel, ruthenium, rhodium, palladium, iridium, rhenium and platinum. Non-limiting examples of suitable support materials include alumina, silica, silica-alumina, titania and cerium oxide—the preferred support material is alumina.

The type of laser radiation used in the process of the present invention is not particularly restricted provided that the radiation is absorbed by the fouled catalyst to be regenerated. For example, the laser radiation may be generated from a laser of the CO_2, YAG or Excimer variety. Preferably, the radiation is generated from a CO_2 laser. The laser radiation may be pulsed, continuous wave (hereinafter referred to as CW) or pulsed CW. Preferably, the radiation is pulsed CW. The most preferred laser radiation is generated from a CW CO_2 laser operated in pulse mode.

Preferably, a particular catalyst particle is exposed to the laser radiation for a period of from about 1 microsecond to about 100 milliseconds, more preferably from about 100 microseconds to about 10 milliseconds. The wavelength of the laser radiation is preferably from about 200 nm to about 10,000 nm, more preferably from about 1,000 nm to about 10,000 nm. Preferably, the laser is operated at a fluence regime of from about 10 to about 1000 J/cm^2, more preferably from about 20 to about 100 J/cm^2. The intensity of the laser beam is preferably from about 10 W/cm^2 to about 1 MW/cm^2.

Embodiments of the invention will now be described with reference to the following Examples which are provided for illustrative purposes and should not be construed as limiting.

LASER REGENERATION OF DEACTIVATED CATALYSTS

A series of experiments were conducted to determine the effects of the present regeneration process on the physical, surface and bulk chemical properties of two different spent commercial hydroprocessing catalysts. Deactivated (fouled) catalyst samples were prepared for laser regeneration by de-oiling in toluene, drying in air at a temperature of from 50° to 70° C. Thereafter, the dried 1/16 inch catalyst extrudates were ground and sieved to a 20–50 mesh particle size.

Oxidative regeneration of the coked catalyst surface was conducted by placing the catalyst particles in a sample holder. Radiation from a CW CO_2 laser was directed on to the particles while an oxidizing gas (in this case air) was passed over the surface of the catalyst particles. The reaction products were flushed out of the sample system allowing replenishment of the air (and thus oxygen) supply to the reaction zone by gas flow. Agitation of the catalyst particles facilitated greater exposure to the laser radiation thereby leading to more efficient coke burn-off.

In these experiments, use was made of a Lumonics VFA 1700 CW CO_2 laser which was operated in a pulse mode with 0.5 ms pulses. The pulse repetition frequency was varied to obtain the desired average power. At a frequency of 1000 Hz the laser power was typically 50 W. Generally, the catalyst regeneration process was conducted at an average power of about 40 W, without focussing. Under such conditions, with a laser beam diameter of 1.4 cm, the laser intensity was about 26 W/cm^2. The catalyst particles were exposed to the laser radiation whereby the batch process time was about one second.

CHARACTERIZATION OF CATALYSTS

Physical characterization of ground catalyst samples before and after deactivation and regeneration was conducted utilizing mercury porosimetry analysis. Thus, using a Micromeritics Auto-Pore 9200 mercury porosimeter, pore volume and pore area of the catalyst were readily determined.

Structural changes to the catalyst surface were detected and observed utilizing a scanning electron microscope (hereinafter referred to as "SEM"). Specifically, use was made of a Hitachi model S520 SEM with a primary electron beam energy of 25 KeV. To avoid charging, catalyst samples were coated with a vapour deposited Au-Pd conductive film approximately 150 Å thick.

Chemical analysis of the catalyst surface was conducted utilizing X-ray photoelectron spectroscopy (hereinafter referred to as "XPS"). Specifically, spectra were recorded with a Surface Science SSX-100 spectrometer using monochromatized Al Kα X-ray radiation with an electron beam energy of 10 kV. The binding energy scale of the spectrometer was calibrated using gold foil (Au $4f_{7/2}$ = 83.9 eV). The samples were mounted on grooved indium foil. The base pressure of the analytical chamber was approximately 10^{-10} Torr.

In addition to using XPS, chemical analysis of the catalyst surface was conducted utilizing proton-induced X-ray emission spectroscopy (hereinafter referred to as PIXE spectroscopy). Specifically, the spectra were recorded using a General Ionex 4 MeV Tandem Accelerator with a proton beam energy of 1.650 MeV and a Si-Li detector. For samples to be tested the beam intensity was set at a count rate of 75 sec^{-1}. The catalyst samples were analyzed "as-is" without further preparation.

Fourier transform infrared (FTIR) spectroscopy was utilized to obtain chemical analysis of the catalyst and

thereby complement the XPS surface analysis discussed above. Specifically, the FTIR spectra were obtained using a Nicolet 20 SX FTIR spectrometer with a diffuse reflectance attachment. Thus, the spectra were obtained at a resolution of about 0.5 cm^{-1} and were the average of 100 scans.

EXAMPLE 1

Co-Mo/γ-Al_2O_3 was designated as Catalyst A, which was deactivated by conducting semi-pilot plant hydrotreating experiments. The catalyst was deactivated (fouled) by severe hydrogenation of a synthetic crude middle distillate fraction according to the following procedure.

The feedstock was distilled from synthetic crude at a boiling range of from 142° to 333° C. 70 g of Catalyst A was loaded into a bench-scale continuous flow reactor and after sulphiding with 10% H_2S in hydrogen for two hours at a temperature of 380° C., liquid feedstock and hydrogen were passed through a mixer and over the fixed catalyst bed. The hydrogen pressure was fixed at 2500 psig and liquid space velocity was varied from 0.75 to 2.25 h^{-1}. The reactor was run for seventy hours during which the temperature was varied from 340° to 440° C. After completion of the run, the catalyst was recovered, de-oiled, ground and sieved to a 20–50 mesh particle size as described above.

Unused, fouled (coked) and laser regenerated samples of Catalyst A were designated Catalyst 1A, 2A and 3A, respectively. The physical characteristics of Catalysts 1A, 2A and 3A were determined by mercury porosimetry and are provided in Table 1. As shown in Table 1, where comparisons are made between Catalyst 1A and Catalyst 2A, the effects of coking are evident in the results for the latter with regard to total pore volume and total pore area. The physical characteristics for Catalyst 3A (laser regenerated) shown in Table 1 indicate that, within experimental error, the total pore volume and total pore area have been completely restored when compared to the respective values obtained for Catalyst 1A (unused).

Reference will now be made to FIGS. 1, 2 and 3 which illustrate scanning electron micrographs of Catalysts 1A (unused), 2A (fouled) and 3A (laser regenerated), respectively. In addition, FIG. 4 is provided and illustrates a laser irradiated unused Co-Mo/γ-Al_2O_3 catalyst (hereinafter referred to as "Catalyst 4A"). From these Figures, it is evident that the surface microstructure of Catalyst 4A is unchanged by laser irradiation alone. Moreover, laser processing of the Catalyst 2A (fouled) to yield Catalyst 3A (laser regenerated) leads to a restored catalyst surface which closely resembles the surface of Catalyst 1A (unused). Thus, micropores visible in the Catalyst 1A (unused) are still present in Catalyst 3A (laser regenerated) and Catalyst 4A laser irradiated unused). From these results, it is apparent that laser regeneration does not significantly alter the morphology of the catalyst surface.

TABLE 1

	Co-Mo/γ-Al_2O_3 CATALYST		
POROSIMETRY DATA	1A-UNUSED	2A-FOULED	3A-LASER REGENERATED
TOTAL PORE VOLUME (mL/g)	0.43	0.33	0.46
TOTAL PORE AREA (m^2/g)	213.0	167.5	195.1
MEDIUM PORE DIAMETER (um)	0.0082	0.0082	0.0093
BULK DENSITY (g/mL)	1.290	1.348	1.241
SKELETAL DENSITY (g/ml)	2.461	2.401	2.449

Surface chemical analysis was conducted on Catalysts 1A (unused) and 3A (laser regenerated) using XPS. The results of this analysis are provided in Table 2. As shown in Table 2, there are no significant differences between Catalyst 1A (unused) and Catalyst 3A (laser regenerated) in the surface concentrations of the active phases (i.e. Co and Mo) or of the support material (i.e. Al and O). The data provided in Table 2 for "C 1s" is representative of the content of carbon contaminant on the catalyst surface. From these results it is apparent that laser regeneration may be used to achieve removal of surface carbonaceous material from the catalyst while leaving the composition of the active surface metal components substantially unchanged.

Reference will now be made to FIG. 5 which illustrates XPS spectra for Catalysts 1A (unused), 3A (laser regenerated) and 4A (laser irradiated unused). As shown in FIG. 5, there is one dominant Mo oxidation state in the region of the Mo 3d binding energy for Catalyst 1A (unused). The position of the $3d_{5/2}$ component of this spin-orbit doublet at a binding energy of 232.8 corresponds to Mo^{6+}. Demanet et al (*Appl. Surf. Sci.*, 14, 271 (1983)) teach that this is indeed the common state of molybdenum in these catalysts after calcining at moderate temperatures (e.g. from 350° to 500° C.) in air. With reference to Catalyst 4A (laser irradiated unused), exposure of unused catalyst to laser radiation did not lead to the formation of new oxidation states or to compounds with Co or with the support material. If such new oxidation states or compounds were formed, one would have expected to observe, for example, peaks at lower binding energy corresponding to $CoMoO_4$ or $Al_2(MoO_4)_3$. With reference to Catalyst 3A (laser regenerated), FIG. 5 illustrates that the regenerated catalyst comprises substantially all of the Mo as Mo^{6+} (i.e. binding energy of 232.8). From these results, it is apparent that laser regeneration of the hydroprocessing catalyst did not result in significant alteration of the catalyst surface.

TABLE 2

SURFACE COMPOSITION (% Relative Intensity) DETERMINED BY XPS SPECTROSCOPIC ANALYSIS					
Co-Mo/γ-Al_2O_3 Catalyst	Co $2p_{3/2}$	Mo $3d_{5/2}$	Al 2p	O 1s	C 1s
1A. (Unused)	0.73	2.98	30.55	58.94	6.80
Unused*	0.55	2.37	30.28	57.20	9.59
3A. (Laser Regenerated)	1.15	2.70	30.24	56.07	9.83

*Duplicate analysis of unused catalyst

The results of PIXE spectroscopic analysis of Catalysts 1A (unused), 2A (fouled), 3A (laser regenerated and 4A (laser irradiated unused) are provided in Table 3. These illustrate that upon fouling, the catalyst bears relatively reduced amounts of support (i.e. Al) and

active (i.e. Mo and Co) phases —compare Catalyst 1A with Catalyst 2A. This is not unexpected since coke fouling adds mass to the catalyst (i.e. carbon and sulphur) thereby reducing the relative amounts of other catalyst constituents. However, upon regeneration according to the present process, the concentration of the active and support phases of the catalyst are restored. Thus, the present process removes surface carbonaceous matter and sulphur contained therein and does not lead to significant changes and/or modifications to the surface concentrations of the active catalytic phases.

changes in the surface concentrations of the active phases (i.e. Ni and Mo) or of the support material (i.e. Al and O).

Reference will now be made to FIGS. 6, 7 and 8 wherein there are illustrated FTIR spectra of Catalysts 1B (unused), 2B (fouled) and 3B (laser regenerated), respectively. As shown in FIG. 6, the spectrum for Catalyst 1B (unused) contains a strong absorption band at about 1000 cm^{-1} and a broad absorption band at about 3600 cm^{-1}. Lipsch et al (*J. Catal.*, 15, 174–178 (1969)) have shown that these two absorption bands are characteristic of MoO_3 supported on γ-Al_2O_3.

TABLE 4

	Ni-Mo/γ-Al_2O_3 CATALYST		
POROSIMETRY DATA	1B-UNUSED	2B-FOULED	3B-LASER REGENERATED
TOTAL PORE VOLUME (mL/g)	0.37	0.25	0.37
TOTAL PORE AREA (m^2/g)	177.3	123.9	119.7
MEDIUM PORE DIAMETER (um)	0.0093	0.0082	0.0123
BULK DENSITY (g/mL)	1.389	1.525	1.412
SKELETAL DENSITY (g/ml)	2.839	2.439	2.975

EXAMPLE 2

Ni-Mo/γ-Al_2O_3 (commercially available as Shell 424) was designated as Catalyst B and was deactivated through use in an industrial hydrotreating unit for upgrading syncrude naphtha coker distillate. Prior to its use in this Example, Catalyst B had been regenerated twice using a conventional industrial oxidative regeneration process. Prior to regeneration, the catalyst had been run for an approximately 18-month cycle in the commercial trickle bed hydrotreating reactor (above) with constant ramping of temperature from about 340° to about 400° C.

TABLE 3

MASS CONCENTRATION (%) DETERMINED BY PIXE SPECTROSCOPIC ANALYSIS					
Co-Mo/γ-Al_2O_3 CATALYST	Al	P	S	Co	Mo
1A	37.91	0.867	1.304	2.965	7.809
2A	34.55	0.848	7.804	2.622	6.887
3A	40.20	0.945	1.675	3.019	7.783
4A	39.93	0.936	1.555	3.144	8.155

Unused, fouled (coked) and laser regenerated samples of Catalyst B were designated as Catalyst 1B, 2B and 3B, respectively. A laser irradiated unused sample of Catalyst B was designated as Catalyst 4B. It should be appreciated that for this Example the used catalyst (Catalyst 2B) was previously regenerated twice. Catalyst 3B (laser regenerated) was prepared by subjecting Catalyst 2B (fouled) to the laser irradiation process described hereinbefore. Prior to chemical and physical analysis, the catalyst was recovered, de-oiled, ground and sieved as described above. The physical characteristics of Catalysts 1B, 2B and 3B were determined by mercury porosimetry and are provided in Table 4. These results indicate the present process can be utilized to substantially or, in some cases, completely restore the total pore volume of the catalyst. It is believed that the loss of total pore area for Catalyst 3B is due substantially to the previous industrial high temperature oxidative regeneration and recycle of the catalyst.

Surface chemical analysis was conducted on Catalysts 1B (unused) and 3B (laser regenerated) using XPS. The results of this analysis are provided in Table 5. As shown in Table 5, these results indicate that laser regeneration of the catalyst did not result in significant

TABLE 5

SURFACE COMPOSITION (% RELATIVE INTENSITY) DETERMINED BY XPS SPECTROSCOPIC ANALYSIS					
Ni-Mo/γ-Al_2O_3 CATALYST	Ni $2p_{3/2}$	Mo $3d_{5/2}$	Al 2p	O 1s	C 1s
1B Unused	0.79	3.39	31.89	55.37	8.56
3B Laser Regenerated	0.52	3.30	31.01	52.13	14.03*

*Strong C 1s intensity was due to contaminant carbon generated in the XPS vacuum chamber

In contrast, the spectrum for Catalyst 2B (fouled), shown in FIG. 7, contains a broad continuum absorption from about 1600 cm^{-1} to about 4000 cm^{-1}. The only other absorption bands apparent in the strong absorption spectrum for Catalyst 2B are a band at about 1000 cm^{-1} which, as discussed above, is characteristic of MoO_3 and a band at about 1650 cm^{-1} which is characteristic of physically absorbed water. Since it is well known that graphitic materials (e.g. coke) are low band-gap, broad band absorbing species, the broad absorption feature of the FTIR spectrum for Catalyst 2B may be attributed to the carbonaceous material on the catalyst surface.

With reference to FIG. 8, the FTIR spectrum for Catalyst 3B (laser regenerated) is very similar to that for Catalyst 1B (unused; see FIG. 6). The spectrum for Catalyst 3B does not contain a peak shift of the MoO_3 characteristic at 1000 cm^{-1}. From these results, it is apparent that laser regeneration of a fouled hydroprocessing catalyst does not significantly alter the chemical nature of the original catalyst.

The results of PIXE spectroscopic analysis of Catalysts 1B (unused), 2B (fouled), 3B (laser regenerated) and 4B (laser irradiated unused) are provided in Table 6. These results illustrate that, upon fouling, the catalyst bears relatively reduced amounts of support (i.e. Al) and active (i.e. Mo and Ni) phases—compare Catalyst 1B with Catalyst 2B. This is not unexpected since coke fouling adds mass to the catalyst (i.e. carbon and sulphur) thereby reducing the relative amounts of other catalyst constituents. However, upon regeneration according to the present process, the concentration of the active and support phases of the catalyst are restored. Thus, the present process does not lead to significant

changes and/or modifications in the surface concentrations of the active catalytic phases.

TABLE 6

MASS CONCENTRATION (%) DETERMINED BY PIXE SPECTROSCOPIC ANALYSIS					
Ni-Mo/γ-Al_2O_3 CATALYST	Al	P	S	Ni	Mo
1B	34.18	3.179	1.654	2.699	10.16
2B	30.05	2.389	8.377	2.103	8.174
3B	36.03	2.970	1.946	2.526	9.183
4B	36.85	3.072	1.505	2.757	9.291

We claim:

1. A process for regenerating a deactivated hydroprocessing catalyst fouled with carbonaceous material, said process comprising the step of regenerating the catalyst by removing substantially all of said carbonaceous material from said catalyst by exposing said catalyst to laser radiation in the presence of an oxidizing gas, wherein said laser radiation has a wavelength of from about 200 nm to about 10,000 nm, a fluence regime of from about 10 to about 1000 J/cm^2 and an intensity of from about 10 W/cm^2 to about 1 MW/cm^2.

2. The process defined in claim 1, wherein said catalyst is in the form of particles.

3. The process defined in claim 2, wherein said catalyst is agitated during exposure to said laser radiation.

4. The process defined in claim 2, wherein the particle size of said catalyst is 20–50 mesh.

5. The process defined in claim 4, wherein said catalyst is agitated during exposure to said laser radiation.

6. The process defined in claim 1, wherein said oxidizing gas comprises from about 15 to about 25 weight percent of oxygen.

7. The process defined in claim 1, wherein said catalyst is a metal supported on a support material.

8. The process defined in claim 7, wherein said metal is selected from the group comprising iron, chromium, cobalt, nickel, ruthenium, rhodium, palladium, iridium, rhenium and platinum.

9. The process defined in claim 8, wherein said support material is selected from the group comprising alumina, silica, silica-alumina, titania, carbon and cerium oxide.

10. The process defined in claim 1, wherein said catalyst is a metal sulphide supported on a support material.

11. The process defined in claim 10, wherein said metal sulphide is selected from molybdenum sulphide and tunsten sulphide.

12. The process defined in claim 11, wherein said metal sulphide is promoted by a compound selected from nickel sulphide and cobalt sulphide.

13. The process defined in claim 12, wherein said support material is selected from the group comprising alumina, silica, silica-alumina, titania and cerium oxide.

14. The process defined in claim 1, wherein said catalyst is selected from the group comprising hydrotreating catalysts, hydrocracking catalysts, gasoline reforming catalysts, catalysts for selective hydrogenation of pyrolysis gasolines, and catalyst supports used as molecular sieves.

15. The process defined in claim 14, wherein said hydrotreating catalysts are selected from the group comprising hydrodesulphurization catalysts, hydrodenitrogenation catalysts and catalysts for hydrogenation of olefins and aromatics.

16. The process defined in claim 1, wherein said laser radiation is generated from a laser selected from the group comprising CO_2, Yag and Excimer.

17. The process defined in claim 1, wherein said laser radiation is generated from a CO_2 laser.

18. The process defined in claim 16, wherein said laser is operated in a mode selected from pulsed, continuous wave and pulsed continuous wave.

19. The process defined in claim 17, wherein said CO_2 laser is operated in pulsed continuous wave mode.

20. The process defined in claim 1, wherein said catalyst is exposed to said laser radiation for a period of from about 1 microsecond to about 100 milliseconds.

21. The process defined in claim 19, wherein said catalyst is exposed to said laser radiation for a period of from about 100 microseconds to about 10 milliseconds.

22. The process defined in claim 21, wherein said laser radiation comprises a wavelength of from about 1,000 nm to about 10,000 nm.

23. The process defined in claim 19, wherein said laser is operated in a fluence regime of from about 20 to about 100 J/cm^2.

* * * * *